Design and Synthesis of Nitrogen-rich Heterocyclic Compounds and Salts as Energetic Materials

A Thesis Submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

Dharavath Srinivas

Advanced Centre of Research in High Energy Materials
University of Hyderabad
Hyderabad – 500 046
INDIA
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to my mother….

మాతృమూర్తి చరణారవిందాలకు
అంకితం.

STATEMENT

I hereby declare that the matter embodied in the thesis entitled "**Design and Synthesis of Nitrogen-rich Heterocyclic Compounds and Salts as Energetic Materials**" is the result of investigations carried out by me in the Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad, India, under the supervision of Dr. K. Muralidharan and it has not been submitted elsewhere for the award of any degree or diploma or membership, etc.

In keeping with the general practice of reporting scientific investigations, due acknowledgements have been made wherever the work described is based on the findings of other investigators. Any omission, which might have occurred by oversight or error, is regretted.

Dharavath Srinivas

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CERTIFICATE

This is to certify that the work described in this thesis entitled **“Design and Synthesis of Nitrogen-rich Heterocyclic Compounds and Salts as Energetic Materials”** has been carried out by **Mr. Dharavth Srinivas**, under my supervision at **Advanced Centre of Research in High Energy Materials**, University of Hyderabad, Hyderabad, India and the same has not been submitted elsewhere for any degree.

Place: Hyderabad
Date:

Dr. K. Muralidharan
(Thesis Supervisor)

Director
ACRHEM

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Thank you, all.

D. Srinivas

August 2014

ACRHEM, Univeristy of Hyderabad

CONTENTS

CHAPTER 1

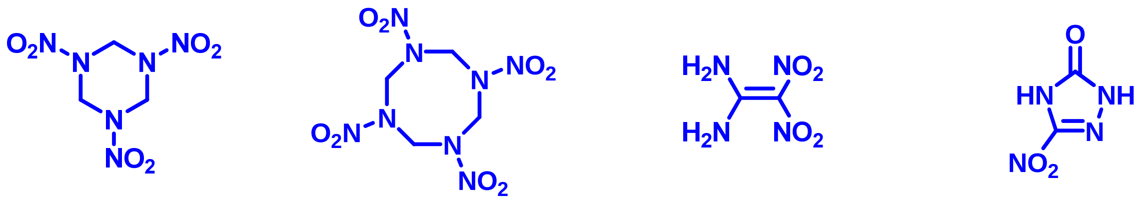
Introduction to Energetic Materials

1.1 History, Background and Definitions

Development of energetic materials, in other words, substances that burn, combust rapidly or explode under certain conditions constitutes one of mankind's early scientific investigations. The entirety of energetic materials is defined by the American Society for Testing and Material as "a compound or mixture of substances which contains both the fuel and the oxidizer and reacts readily with the release of energy and gas" [1]. Explosives are most often vaguely expressed as a solid or liquid substance (or mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Energetic materials encompass various chemical compositions of fuel and oxidant that react rapidly upon initiation and release large quantities of force or energy [2].

The chemistry of explosives, their development and application are as old as 220 years BC [3]. It is generally acknowledged that black powder was invented by the Chinese and was primarily used for fireworks. Although the history of energetic materials is well chronicled in the literature [4] a small look at milestone developments should be discussed. Black powder and other early energetic material were mostly used for fireworks, but their potential use as propellants for small and middle caliber weapons was also recognized quickly. The first high explosive discovered was probably nitrocellulose (also known as gun-cotton) but its development was long delayed by difficulties in obtaining a stable product. Sensitivity was always an issue with the production of nitroglycerine and many accidents occurred during its preparation. Hence, we see one very important property of high explosives, the ability to explode while certain outer stimuli are applied. The period leading up to the First World War also saw the birth of modern explosives. The much less sensitive trinitrotoluene (TNT) was also invented in the 19th century and replaced the common picric acid in most weapon systems. TNT was used as the standard explosive in one of the world's biggest armed conflicts, the 1st world war, while the later invented hexogen (RDX) fared as the standard explosive in the 2nd world war. An understanding and application of energetic materials in conflict has served, throughout history, as the key technological advantage of one civilization over another. In our modern times, not only the application for warfare is studied, but the utilization of energetic materials for civilian use in mining, construction, demolition and safety equipment such as airbags, signal flares and fire extinguishing systems is extensively studied.

"*One of the biggest steps for mankind would have been impossible without the development of energetic materials*".

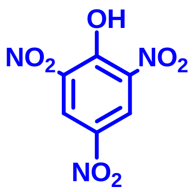


RDX *HMX* *FOX-7* *NTO*

***Figure 1.1**. Common energetic materials*

Energetic materials are divided into three unique classes: Explosives, Propellants and Pyrotechnics. Since this work focuses on chemistry of energetic materials, these compounds have to derive their energy from chemical reactions, not from physical or nuclear reactions. The *physical explosion* is a result of a formed pressure within a container or vessel, often by compressed or heated liquids or gases, leading to a sudden expansion of the gases when the container or vessel fails. The compressed gases, along with fragments of the burst container, can lead to severe, damaging effects. The *nuclear explosion* can, as well, be understood as a physical

TNT



Picric acid

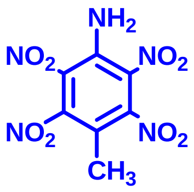
Picramide

Trinitroanisole

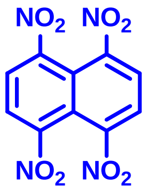
TATB

TNPG

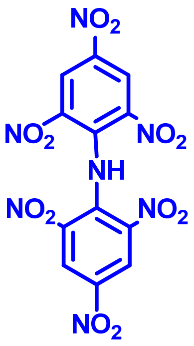
2,3,4,5,6-Pentanitroaniline



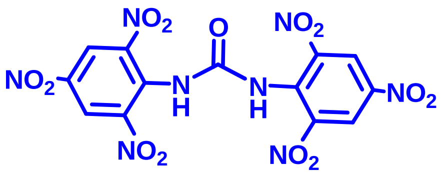
4-Amino-2,3,5,6-tetranitrotoluene



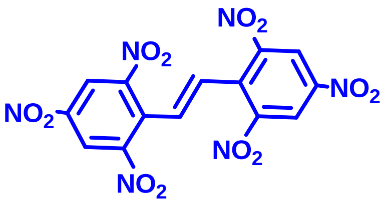
1,4,5,8-Tetranitronaphthalene



2,2',4,4',6,6'-Hexanitrodiphenylamine (hexyl)



,2',4,4',6,6'-Hexanitrocarbanilide



2,2',4,4',6,6'-Hexanitrostilbene (HNS)

Figure 1.2. *Energetic nitroarenes*

explosion, due to the radioactive elements, which are driven together by common explosives (energy supplied from outside the system). Nevertheless, the explosive energy of a nuclear explosion is derived from the transmutation of the radioactive substance into different elements and tremendous amounts of energy. The power obtained by nuclear explosion exceeds the energies of chemical or physical explosions. The *chemical explosion* is a result of the decomposition of molecules evolving gases and heat. The burning rate of the chemical compound determines whether the decomposition is just a burning, a deflagration or a detonation. The explosion can be caused either by direct initiation or by a deflagration to a detonation process.

The class of explosives can be divided further into primary and secondary explosives [5]. Primary explosives like lead azide, which is commonly used in blasting caps, are highly sensitive materials that can be ignited by small physical stimuli of mechanical, electrostatic or thermal nature. They usually don't exhibit very high performance values but undergo a rapid transition from deflagration to detonation. Their detonation velocities ranging between 3500 m/s and 5500 m/s are much slower than the detonation velocities of secondary explosives. Common primary explosives are lead(II)azide, lead(II)styphnate, cadmium(II)azide and mercury fulminate. The obvious disadvantage of these compounds is the toxicity of the heavy metal cations lead, cadmium and mercury. Therefore, new less toxic primary explosives based on organic, metal free compounds were investigated and developed and has future scope. Secondary explosives on the other hand cannot be ignited by the same stimuli as primary explosives since they are not only much more stable in terms of friction, impact and electrostatic discharge but also kinetically stable (metastable) compounds and hence they have to be ignited by much larger stimuli. The main differences between the secondary explosives and the primary explosives are the high thermal and physical stability of the secondary explosives along with higher detonation velocities (5500 m/s to 9500 m/s). Normally the energy needed for the initiation of secondary explosives is generated by the detonation shockwave of primary explosives. Although they need a much higher impetus to be detonated, secondary explosives exhibit much higher performances (release more energy per time) than primary explosives.

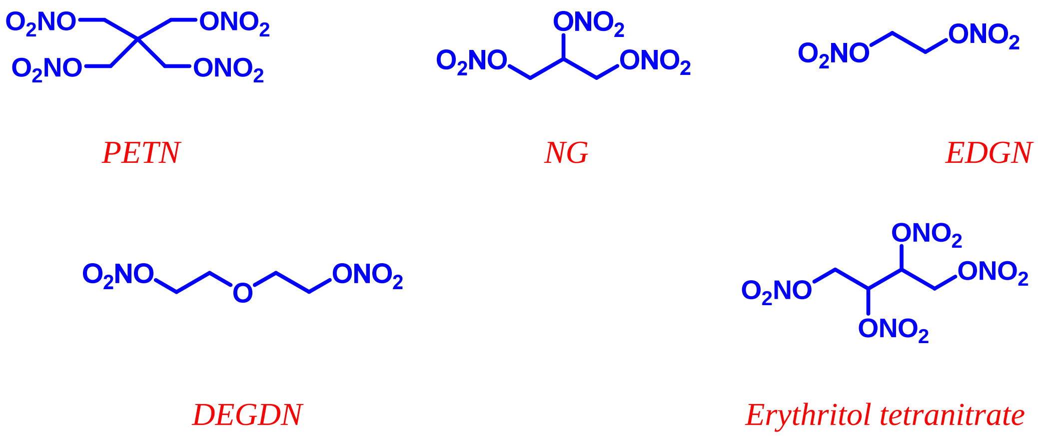
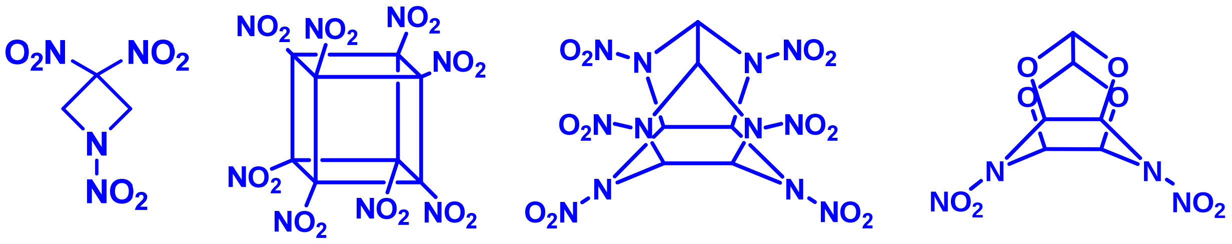


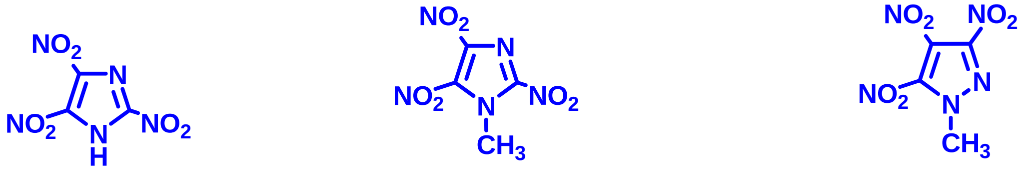
Figure 1.3. Chemical structure of selective energetic nitroesters

Propellants on the other hand are energetic materials consisting of single compound which is a fuel and also have oxidizer group witin its structure, or a separate mixture of a fuel and an oxidizer [6]. They combust or deflagrate very fast releasing a high amount of gas and energy (heat, combustion temperature), sufficient enough to increase the temperature and the pressure of the surroundings and finally providing propulsive force (specific impulse) in order to lift defined payloads. Pyrotechnic compositions are not known primarily for the transfer of stored chemical energy into kinetic energy to the surroundings, but use the stored chemical energy for the purpose of generating "pyrotechnical" effects, either of visual or accustic nature [7]. Pyrotechnics can be divided into three fields, the heat generating, the smoke generating and the light emitting pyrotechnics. Heat generating pyrotechnics are used for priming charges, detonators, incendiary compositions or matches. Smoke generating pyrotechnics are used for camouflage and signaling purposes. The light emitting pyrotechnics are used either for illumination (visible and infrared), fireworks or decoy flares. The discussion of pyrotechnic systems is omitted, since the primary objective of this thesis is the synthesis and characterization of secondary explosives and, to a certain extent, propellant systems.

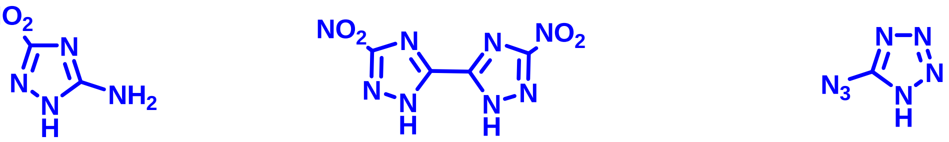


TNAZ *ONC* *CL-20* *TEX*

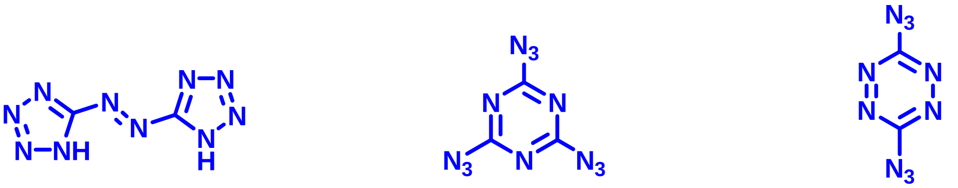
Figure 1.4. *Energetic cage and strained compounds.*



2,4,5-trinitro-1H-imidazole *1-methyl-2,4,5-trinitro-1H-imidazole* *1-methyl-3,4,5-trinitro-1H-pyrazo*



3-nitro-1H-1,2,4-triazol-5-amine *5,5'-dinitro-2H,2'H-3,3'-bi(1,2,4-triazole)* *5-azido-1H-tetrazole*



(E)-1,2-di(1H-tetrazol-5-yl)diazene *2,4,6-triazido-1,3,5-triazine* *3,6-diazido-1,2,4,5-tetrazine*

Figure 1.5. *Energetic compound composed of heterocyclic rings*

The chemical reaction of the energetic materials defines their application. Propellants are usually combusted to deliver high amounts of gaseous products at high temperatures in order to deliver high pressure and subsequently a high velocity of the detonation products. Combustions or burning reactions are the slowest reactions that occur in energetic materials and are defined as self-propagating oxidation reactions, either performed on air or by an oxidizing function. Two different chemical processes are known for secondary as well as for primary explosives, both of them being much faster than normal combustions. Secondary explosives on the one hand can undergo a deflagration if they are not used in confined spaces. This means, that the reaction proceeds on the surface of the material at slightly subsonic linear velocities, mostly propagated by heat transfer and moves from there through the unreacted material. A detonation on the other hand is not propagated by heat transfer, but by a supersonic shockwave travelling through the unreacted material, hence representing the fastest release of chemical energy known. The reaction is always sustained by the rapid release of energy behind the wave-front and is normally observed under strong confinement of energetic materials or if initiated by the shockwave from a primary explosive. Performance of explosive materials is most simply notated by the detonation velocity (*VOD*) and detonation pressure (*DP*). The detonation velocity is the speed at which the shockwave and chemical reaction zone propagates the reaction within an explosive material. The detonation pressure is calculated at the Chapman-Jouguet plane [8], the hypothetical plane behind the shockwave front that separates the zone following the chemical reaction zone immediately after the wave front and the zone where chemical reaction products are free to expand.

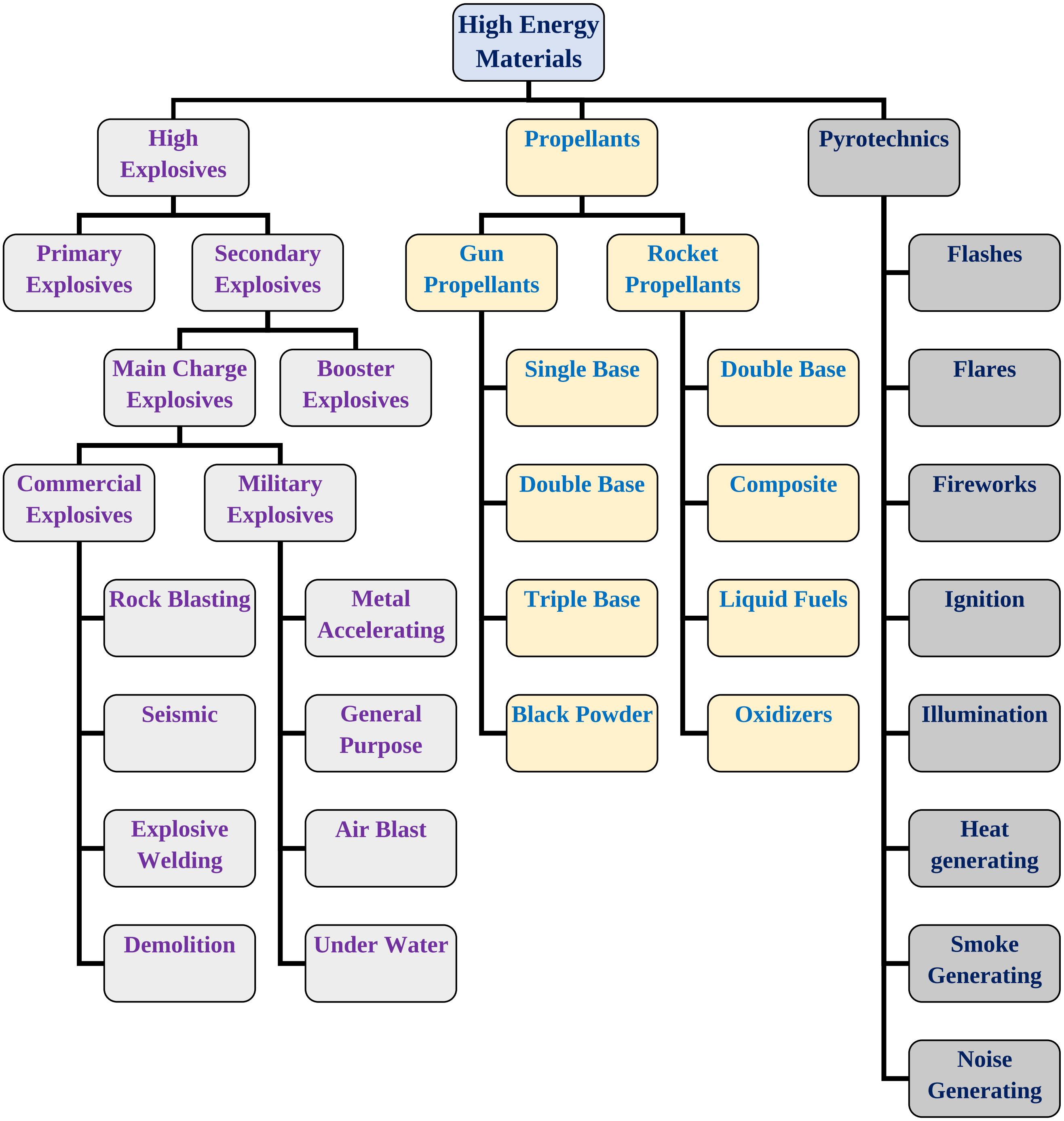


Chart 1.1: Clasification of energetic materials

Almost all reactions of explosive substances proceed exothermally. This means that explosives need to have chemical groups in their molecules that increase their heats of formation and produce gaseous products upon reaction. This type of chemical groups is called explosophores. The most famous explosophoric groups are based on nitrogen and oxygen, such as the classical nitro, nitrate, nitrate ester, nitramine and azido groups. Also well known are perchlorates and chlorates. Due to the presence of these explosophoric groups, the oxygen needed for the conversion of explosives into their gaseous reaction products such as NO_x, CO_2, CO and H_2O are available within the concerened molecules. This prerequisite becomes more and more important when a chemical reaction proceeds faster since the diffusion process in the air is no longer efficient enough to deliver sufficient amounts of oxygen for the chemical conversion. The nitrogen of explosophoric groups strongly supports the gas production rate as does the chlorine in chlorates and perchlorates.

The rate of energy release can be modified by additives or by varying the concentrations of fuel and oxidizer. The response of the energetic material can be affected by the manner in which it was processed. The properties and behavior of the material can change over time. The rate of the conversion of the material is strongly dependent on the conditions of the initiation. For example, an explosive can be ignited to burn, a process that can be thought of as a reaction wave that proceeds through the material at subsonic speeds or it could be shock-initiated to detonation, where detonation can be described as a reaction wave that proceeds through the material at supersonic speeds. For these cases, the product concentrations and species are not the same. Also, these processes often occur under extreme conditions of temperature and pressures, making experimental measurement difficult. These are but a few of the complexities associated with studies of reactions of energetic materials that make resolving the individual details so difficult. *They are also the reason that research in the field of energetic materials is so exciting!* These difficulties have required the development of a variety of innovative theoretical methods, models and experiments designed to probe details of the various phenomena associated with the conversion of energetic materials to products. Probably the majority of experimental and theoretical efforts in energetic materials research to date have been directed toward assessing performance. The focus is often on quantifying the amount of energy that is released, identifying key reaction mechanisms, or investigating ways in which the energy release can be manipulated and controlled. However, increased environmental and safety concerns are placing new emphases on understanding other aspects of energetic materials, such as toxicity, processing emissions, combustion emissions, wear and erosion on combustion fixtures from reaction products, contamination of ground water or soil, environmentally-friendly synthesis and processing, destruction or disposal, life-span (chemical stability), storage, handling, or vulnerability to a variety of external stimuli.

1.2 Properties of energetic materials

1.2.1 Oxygen balance (OB): It is defined as the ratio of the oxygen content of a compound to the total oxygen required for the complete oxidation of all carbon, hydrogen and other oxidisable elements to CO_2, H_2O, etc and is used to classify energetic materials as either oxygen deficient or oxygen rich. Most energetic materials are oxygen deficient. The most favorable composition for an explosive can be easily calculated from the oxygen values of its components. Commercial explosives must have an oxygen balance close to zero in order to minimize the amount of toxic gases, particularly carbon monoxide and nitrous gases, which are evolved in the fumes. The oxygen balance (O.B.) is calculated from an explosive having the general formula $C_aH_bN_cO_d$ with molecular mass M.

$$\mathrm{OB}\,(\%) = \frac{(\mathrm{d} - 2\mathrm{a} - \mathrm{b}/2) \times 1600}{\mathrm{M}}$$

e.g. TNT ($C_7H_5N_3O_6$) -74%, Nitroglycerine ($C_3H_5N_3O_9$) +3.5% and Ammonium nitrate (NH_4NO_3) +20%.

1.2.2 Heats of Formation: It is the heat of reaction or enthalpy change involved in making a particular compound, or a molecule, from its elements where both the elements and final compound are at standard state conditions. It can be described as the total heat evolved when a given quantity of a substance is completely oxidized in an excess amount of oxygen, resulting in the formation of carbon dioxide, water and sulfur dioxide. For explosive substances which do not contain sufficient oxygen in its molecule for complete oxidation, (e.g. TNT) products such as carbon monoxide, carbon and hydrogen gas are formed. The value for the heat of formation can be negative or positive. If the value is negative, heat is liberated during the reaction and the reaction is exothermic; whereas, if the value is positive, heat is absorbed during the reaction and the reaction is endothermic. For reactions involving explosive components the reaction is always exothermic. In an exothermic reaction the energy evolved may appear in many forms, but for practical purposes it is usually obtained in the form of heat. The energy liberated when explosives deflagrate is called the heat of deflagration, whereas the energy liberated by detonating explosives is called the heat of detonation in kJ/mol or the heat of explosion in kJ/kg.

1.2.3 Density: The density, or more precisely, the volumetric mass density, of a substance is its mass per unit volume. It has been referred [9] as the primary physical parameter in detonation performance because detonation velocity and pressure of the explosives increase proportionally with the packing density and square of it, respectively. An increase in density is also desirable in terms of the amount of material that can be packed into volume-limited warhead or propulsion configurations.

1.2.4 Deflagration and Detonation: Deflagration is an intermediate reaction state between burning and detonation. Energetic material with a large surface area can develop into deflagration. A deflagration reaction is physically unstable and therefore hard to control. Whether the reaction is accelerated further to supersonic velocities and so to a detonation, or the reaction decreases again to burning, depends strongly on the type of explosive, its surface area in this moment and its confinement. Detonation is a chemical reaction given by an explosive substance in which produces a shock wave [10]. High temperature and pressure gradients are generated in the wave front, so that the chemical reaction is initiated instantaneously. Detonation velocities lie in the approximate range of 1500 to 9000 m/s; slower explosive reactions, which are propagated by thermal conduction and radiation, are known as ‘Deflagration’. The burning as well as the deflagration reaction is based on heat transfer. The mechanism of a detonation is triggered by a supersonic shock wave, traveling through the explosive material.

1.2.5 Detonation Velocity and Pressure: Performance of explosive materials is most simply notated by the detonation velocity and detonation pressure. The detonation velocity is the speed at which the shockwave and chemical reaction zone propagates the reaction within an explosive material. The detonation pressure is calculated at the *Chapman-Jouguet* plane [11], the hypothetical plane behind the shockwave front that separates the zone following the chemical reaction zone immediately after the wave front, and the zone where chemical reaction products are free to expand. Detonation velocities of explosives can reach over 10.0 kms^{-1} and detonation pressures can exceed 400 kbar. Unfortunately, while detonation velocities can be measured experimentally, detonation pressures cannot be, however the pressure can be qualitatively correlated to experimental measures of the brisance. Brisance is the shattering power of an explosive and can be relatively correlated to the detonation pressure based on the cutting, denting, or fragmentation of a metal object by an explosive.

1.2.6 Heat of Explosion : The energy released from the chemical reaction that occurs during the burning of propellant or detonation of explosive is called the heat of explosion or heat of detonation. The heat of explosion of an explosive material, an explosive mixture, gunpowder or propellant is the heat liberated during its explosive decomposition. Its magnitude depends on the thermo-dynamic state of the decomposition products; the data used in practical calculations usually have water (which is a product of the explosion) in the form of vapor as the reference compound. The heat of explosion may be both theoretically calculated and experimentally determined. The calculated value is the difference between the energies of formation of the explosive components (or of the explosive itself if chemically homogeneous) and the energies of formation of the explosion products. The advantage of the calculation method is that the results are reproducible if based on the same energies of formation and if the calculations are all conducted by the same method; this is often done with the aid of a computer. The calculated values do not exactly agree with those obtained by experiment. This is because if the explosion takes place in a bomb, the true compositions of the explosion products are different. Further they also vary with the loading density.

1.2.7 Safety characterization: The safety characterization of explosive materials is described in terms of their sensitivity towards mechanical, thermal, and electrostatic stimuli. Mechanical sensitivity is divided into sensitivity towards impact and frictional forces. The impact sensitivity is measured in Joules and is determined by the dropping of masses from various heights upon an explosive confined within a steel sleeve between two rollers. The energy at which one out of the six samples gives an audible or visible decomposition is recorded as the sensitivity (BAM method) [12]. In the case of the measurement of sensitivity towards friction, a small quantity of explosive is placed between two ceramic pieces of controlled frictional coefficients. A weight is applied to the upper ceramic unit and the lower plate is scraped under this. The force (in Newton's) at which one out of six samples gives an audible or visible decomposition is recorded as the sensitiveity. Generally primary explosives are far more sensitive than secondary explosives. Thermal properties of explosives are determined by TG-DTA or DSC. In DSC a sample of explosive is heated at a known rate and the temperature of the explosive is measured relative to a reference. Endothermic events such as melting point or loss of hydration waters and exothermic events such as decomposition are easily determined. Finally, electrostatic sensitivity is measured by sending a spark of known electrical energy through a sample of explosive and the minimal energy for decomposition is recorded.

Table 1.1: Energetic properties of selective energetic materials

Compd.	**OB (%)**	**HOF ($kJmol^{-1}$)**	**ρ ($g\ cm^{-3}$)**	**VOD (kms^{-1})**	**DP (GPa)**
TATB	-56	-138	1.94	8.11	31.1
TNAZ	-17	2	1.84	8.60	35.6
CL-20	-11	454	2.04	9.58	46.6
TEX	-42	-25	1.99	8.56	31.4
HMX	-22	75	1.91	9.10	39.5
FOX-7	-22	-133	1.88	9.09	36.6
NTO	-25	-117	1.93	8.56	31.2
ONC	0	594	1.98	10.10	50.0

1.3 Requirements for Modern Explosives

Before we discuss the requirements necessary for novel explosives, we have to discuss the most common physical as well as chemical properties of these materials and the disadvantages of the classical explosives. The significant properties of energetic materials are oxygen balance, heat of formation, density, detonation performance, thermal stability and sensitivity. Chemical substances are described at first by chemical composition and molecular structure together with their decomposition point (T_{dec}). From the chemical composition, we are able to determine the oxygen balance of a material or the nitrogen content while the molecular structure determines the connectivity between atom density (ρ) and hence the energy of formation of the material. The high energy of formation and the density of the material are the key values which affect the detonation parameters of energetic compounds. The detonation parameters (detonation velocity and pressure) can either be measured or calculated by Kamlet-Jacobs equations [13] or certain programs like EXPLO5 or Cheetah. Just as performance is related to the chemical properties of energetic materials, so is sensitivity. The sensitivity of an explosive substance is a direct reflection of the ability of that substance to dissipate sudden energetic input, without undergoing decomposition (detonation, deflagration or combustion). The ability to dissipate energy without breaking chemical bonds (decomposition) is directly related to the density (lower density materials can dissipate energy more efficiently), molecular structure (certain functional groups are more susceptible to decomposition) and intermolecular interactions within the material (strong interactions between molecules lead to more efficient dissipation of energy).

Classical secondary explosives like 2,4,6-trinitrotoluene (TNT), nitroglycerine (NG) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) show different performance characteristics and reaction pathways for decomposition. TNT and NG derive all their energy from the oxidation of the carbon backbone, which works very well in the case of nitroglycerine, while TNT has a negative oxygen balance and hence much material remains unreacted during explosion. Both compounds exhibit negative heats of formation and hence much lower performance rates than RDX. RDX obtains its energy from the oxidation of the carbon backbone as well from the formation of dinitrogen due to the N–N bonds in the nitramine moieties. Due to the presence of N–N bonds within the nitramine moieties, a positive heat of formation is induced which results, together with the higher density, in significantly higher performance values. The chemical structures of TNT, NG and RDX are compiled in Figures 1.1, 1.2 and 1.3. From the examples of TNT and RDX, we are able to recognize the features necessary for modern explosives. They should have high positive heats of formation paired with high densities and more balanced oxygen balances. The density of materials is hard to be predicted, but it has been proved that introduction of nitro groups in a molecule increases its density [14]. Therefore, the introduction of nitrogen either by catenation through heterocyclic ring systems, by introducing nitro and azido groups, or in the form of nitramine group is a good starting point for the development of novel materials.

Table 1.2. *Energetic properties of NG, TNT and RDX.*

	NG	TNT	RDX
T_m (°C)	13	80	204
T_{dec} (°C)	200	300	-
N (%)	18.5	18.5	37.8
OB (%)	3.5	-73.9	-21.6
ρ (g cm^{-3})	1.59	1.65	1.82
HOF (kJ/mol)	-349	-49	89
Impact sensitivity (J)	0.2	15	7.5
Friction sensitivity (N)	>360	353	120
VOD (kms^{-1})	7.6	6.9	8.75

Another very important point is the cage strain eminent in heterocyclic ring systems and structures. This was based on the fact that the compounds of this family have high strain energies locked in the molecules. Steric strain is represented by increased positive heat of formation as compared with a corresponding unstrained system and release of as extra energy on detonation. The increased strain in the ring shows substantial weakening of the bonds of ring. However, the large bond angle deformations in the ring makes it power house of stored energy and each bond can be thought as storage site for potential energy. They also possess rigid and highly compact structures which decrease the molecular motion and results in increased density. These concepts led to new materials over the last decade [15]. Strained cage and ring systems have been developed like TEX (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane), CL-20 (2,4,6,8,10,12-hexanitro-hexaazaisowurtzitane), ONC (octanitrocubane) and TNAZ (1,3,3-trinitroazetine), while catenated nitrogen systems are also well under investigation like DNAT (5,5'-dinitro-3,3'-azo-1,2,4-1H-triazole). (Figure 1.2). Heterocycles that contain large amount of nitrogen are relatively dense and they possess higher heat of formation because the high percentage decomposition products are usually dinitrogen. Such compounds are classically energetic and release large amounts of energy on combustion and often exhibit high performance. The high nitrogen content of these compounds often leads to a high crystal density which is itself associated with increased performance [16].

Additionally, when talking about the synthesis of new energetic materials, the environmental aspect is most important. The concept of nitrogen catenation is also being utilized in the new area of "Green" energetic materials. Since classical nitro CHNO explosives are not particularly environmentally benign, one of the major goals of green energetic materials research is the development of nitro-free energetic materials. RDX as well as TNT show a high aqua toxicity while disposing them to the environment and hence they are increasingly becoming a soil and ground water contaminant. Another major goal is the replacement of hydrazine containing liquid mono and bipropellants and of environmentally detrimental liquid (N_2O_4) and solid (NH_4ClO_4) oxidizers by more benign materials. The by-products of more environmentally friendly nitrogen-rich energetic materials should be mainly, if not exclusively, molecular nitrogen, carbon dioxide and water. Hence, the development of environmentally friendly compounds which are completely consumed within the process of detonation should be favored.

Factors which must be considered when assessing whether such materials will find practical application include the following:

- Availability of raw materials and price
- Performance
- Sensitivity
- Process ability
- Compatibility
- Chemical and thermal stability
- Temperature-dependent mechanical behavior
- Burn rate and pressure exponent

1.4 Role of Heterocyclic rings in High Energy Materials

The achievement of ‘high performance’ for warhead applications is always an aim of explosive researchers. Heterocycles that contain large amount of nitrogen are relatively dense, they possess higher heat of formation due to higher percentage decomposition products usually dinitrogen [17]. Such compounds are classically energetic and release large amounts of energy on combustion and often exhibit high performance. The high nitrogen content of these compounds often leads to a high crystal density which is itself associated with increased performance. Five member nitrogen containing rings such as imidazole, pyrazole and triazole are the natural framework for energetic materials as they possess high nitrogen content [18] and since the N-N bonds in the ring are stabilized by pseudo aromatic electron delocalization and therefore relatively insensitive. Their performance can be optimized and improved by substituting hydrogen atoms with explosophore like nitro, amino, azido etc. Among various explosophores, nitro group is a vital constituent of energetic materials. The performance of the polynitro compounds is enhanced by excellent oxygen balance which results in a higher exothermicity of the combustion and detonation process. Hence in the search of novel HEDMs, nitro azoles expected to be promising candidates. We mainly focused on the azole based energetic compounds due to their high nitrogen content, availability of starting materials and straight forward synthetic routes.

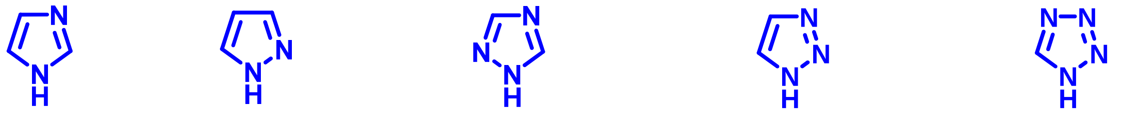


Figure 1.6. Commonly used azoles in energetic materials.

Incorporation of a triazole ring into a compound is a known approach for increasing the thermal stability. Analyses of the structures and properties of a large number of energetic materials reveal that a combination of amino and nitro groups in a molecule often leads to better thermal stability, lower sensitivity to shock and impact and increased explosive performance because of an increase in crystal density. Such observations are attributed to both inter-molecular and intra-molecular hydrogen bonding interactions between adjacent

Amino and nitro groups. Modern triazole-based explosives have been designed and synthesized with this strategy. A further approach is the use of nitrogen-rich heterocycles, particularly, the class of tetrazole derivatives. Tetrazoles are aromatic heterocycles containing one carbon atom as well as four nitrogen atoms. The most elementary tetrazole is 1,2,3,4-1*H*-tetrazole. Due to the delocalization of its electronic system and a [1,5]*H*-shift two main tautomers can be observed: 1*H*-tetrazole and 2*H*-tetrazole. The 5*H*-tetrazole tautomer has never been detected since its loss of aromaticity. Most of the tetrazoles are stable at room temperature. The melting points of 5-monosubstituted tetrazoles are higher than that of the corresponding 1,5- and 2,5-disubstituted homologues due to the formation of hydrogen bonds at the cyclic NH-group.

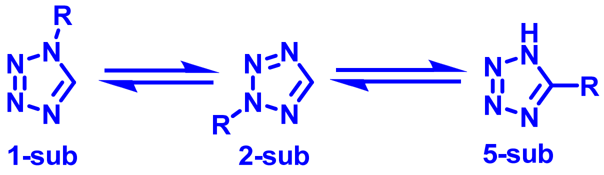


Figure 1.7. Mono substituted tetrazoles.

Another important point of view is the environmental compatibility of the energetic material. Despite the detonation of the explosive composition, a certain amount of unreacted material will be left and widespread in the surrounding area. Owing to our responsibility to protect the environment to our best, the remaining particles after an explosion (the direct damage to the nature when performing an explosion is inevitable, except the explosion is not initiated) should not be toxic or at least less toxic. Therefore, tetrazoles and triazoles represent a “green” alternative, because the decomposition products are only molecular nitrogen and CO/CO_2.

1.5 Concept and Goals

Development of new high explosives - A never ending challenge! Ongoing worldwide research of new energetic materials for both civilian and military applications are; developing pyrotechnics with reduced smoke and new explosives and propellants with higher performance or enhanced insensitivity to thermal or shock stimuli. The introduction of a new compound into practical application is hard (or harder) as commercial launch of new pharmaceuticals. Numerous requirements must be fulfilled, which are not conceivable when designing and synthesizing new energetic materials. One approach is the use of high nitrogen or all-nitrogen compounds. Till the date, there is no example of a homo-polyatomic nitrogen compound which could be used as high energy density materials, since neither thermodynamic nor kinetic stabilization with respect to decomposition into N_2 has been achieved.

The general area of this thesis is the synthesis and complete characterization of novel secondary explosives and, to a certain extent, propellants. The concept of new green energetic compounds as explained above is thereby the main topic of this work. The benefits of the development of new high energy density materials with a high nitrogen content paired with high positive heats of formation are improved performance and also environmental compatibility. Further, these environmentally friendly compounds must exhibit also high thermal stabilities for better and safer handling.

In this context, three classes of heterocyclic systems have been intensively studied, *1H*-benzotriazole, 1,2,4-triazole and tetrazole and their derivatives. Along with these heterocycles, we also studied the energetic salts of 3, 5-dinitropyridin-2-ol, and nitrated phenol derivatives. *1H*-benzotriazole is a well-known fused heterocycle and show wide applications. Fused heterocyclic compounds with reduced vulnerability, low shock and impact sensitivities and increased detonation performance can perhaps form a library of compounds for performance evaluation. As a consequence, the nitrogen-rich fused rings have been widely synthesized and theoretically studied for their energetic performance [19].

Fused rings, such as pyrazolo–pyrazole [20], tetraazacyclooctatetraene (TACOT) [21], benzofuroxans [22] and s-heptazine [23] have been synthesized. We are interested in benzotriazole-based energetic compounds to seek more powerful, less sensitive, ecofriendly energetic materials. Our approach is the use of nitrogen-rich heterocycles, particularly the class of triazole and tetrazole derivatives attached on benzotriazole. Both these heterocycles have the outstanding property of often combining high nitrogen content with good thermal and kinetic stabilities due to their aromatic ring system. These heterocyclic compounds form a unique class of energetic materials whose energy is derived from their very high heats of formation rather than from the overall heat of combustion. The enthalpy criteria of energetic materials are governed by their molecular structure. A scanning of heterocycles with a higher nitrogen content from imidazole (HOF = 129.5 KJ/mol) over 1, 2, 4-triazole (HOF = 192.7 kJ/mol) to tetrazole (HOF = 326.0) the trend in the heats of formation is obvious. The high heat of formation is directly attributable to the large number of energetic N–N, N–C and N–O bonds. Especially energetic ionic salts of tetrazoles have been utilized in energetic roles owing to their higher heats of formation, density and oxygen balance compared to those of their carbocyclic analogues.

In recent years, much attention has been given to the design and development of energetic salts containing nitrogen-rich heterocycles. Because of their structures, energetic salts have unique properties. The properties of the individual components of such salts can also be modified independently by changing the substituents. The choices of cations and anions are usually nitrogen-rich heterocycles that contain various explosophores. This is because these materials combine high energy content with better performance and reduced sensitivity to shock, friction and electrostatic discharge.

The chemistry of polynitroarenes have been widely studied and used in civil as well as military applications due to their remarkable properties. Benzene compounds having three or more nitro groups, exhibit distinctly marked explosive properties (e.g. 2-methyl-1,3,5-trinitrobenzene (TNT), 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitroaniline (picramide) 2,4,6-trinitroanisole, 1,3-diammino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), etc.). Nitro group is important source of oxygen in nitroarenes and most of these compounds release energy mainly from the oxidation of hydrocarbon backbone. Thus, combination of these compounds with heterocyclic compounds expected to modify energetic properties. Previously, few salts of phenolate have been reported [24]. Salts of picric acid with ammonium, guanadinium, or heavy metal cations represented promising properties for applications in military charges and in initiating mixtures. Nitrophenols have limited applications in energetic materials as they are known to react with surrounding metals to yield very sensitive compounds. To overcome this issue, we used nitrophenols in salt formation and to stabilize the materials through the formation of hydrogen-bonded networks. Similarly, potential of the pyridine derivatives in generating the energetic materials with good performance and reasonable thermal stability has been reported. However, to the best of our knowledge, the pyridine based salts are not been explored for their possible application as energetic materials.

Real time performance evaluation of any compound produced requires it in large quantity. However considereing the safety issues, availability of facility for testing and cost involed, the performance of the compounds are normally evaluated by well proven computational method through ab-inito calculations. Thus throught the thesis, the performance of all compounds are evaluated by computations with the help of a colabrator. The computational details are provided in Annexure-I.

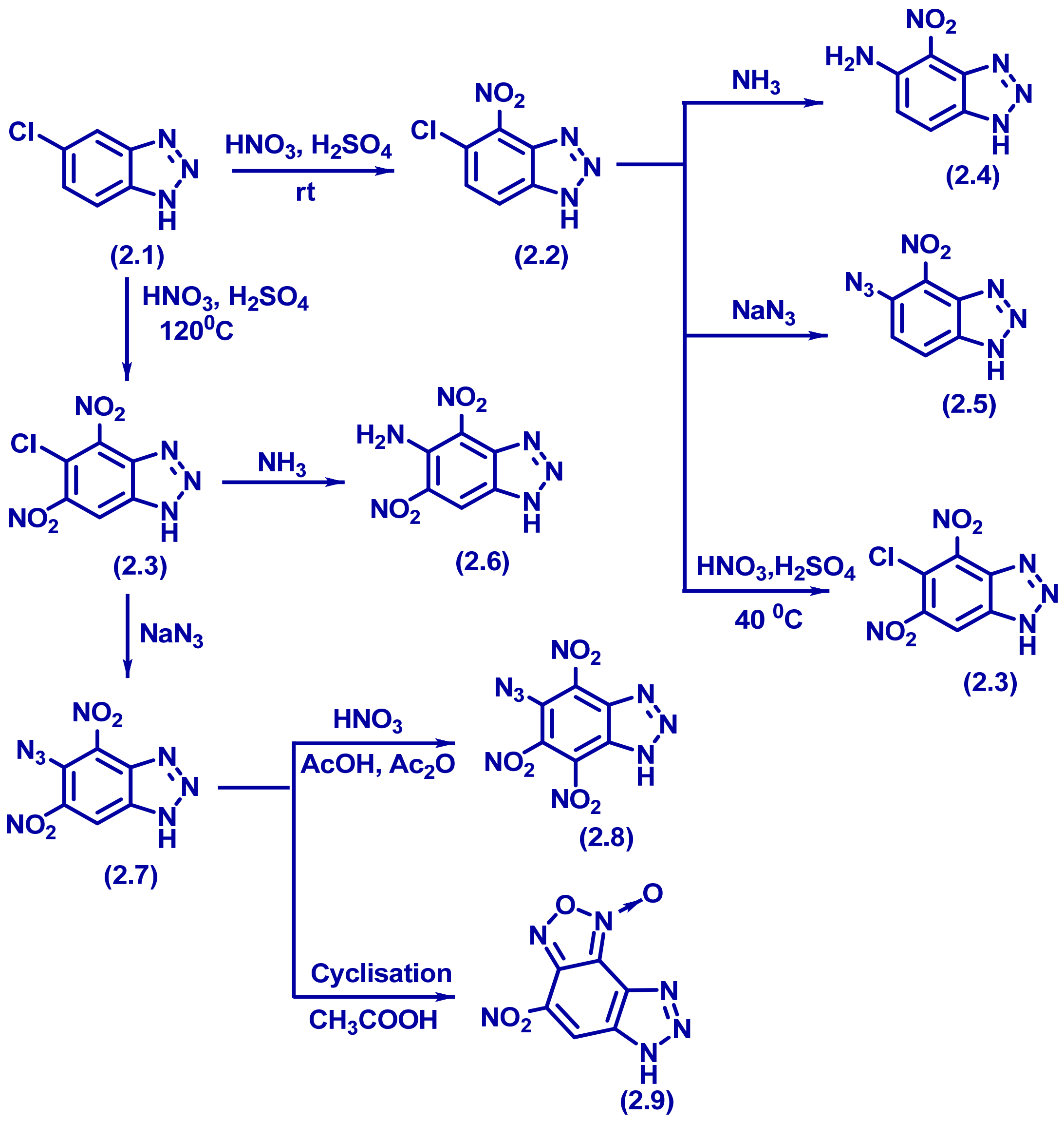
"It is hoped that the works presented in this thesis will stimulate further investigations and advances in the area of energetic materials research".

1.6 Outline of the Chapters

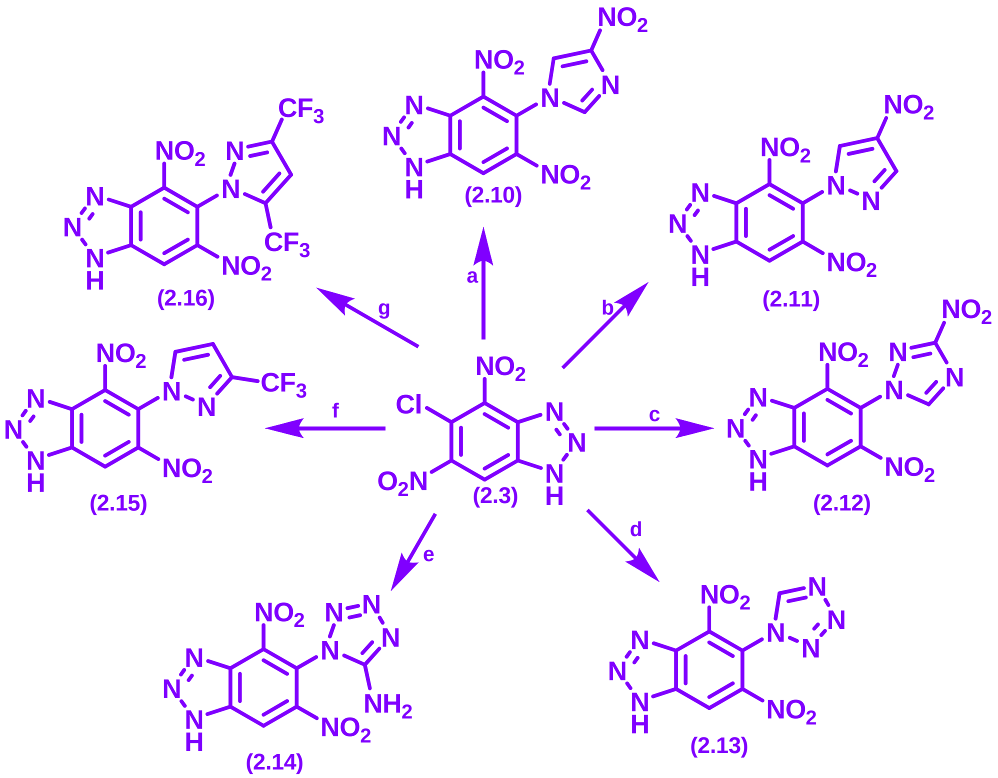
Chapter 2: Synthesis of Amino, Azido, Nitro and Nitrogen-rich Azole Substituted Derivatives of 1*H*-Benzotriazole for High Energy Materials Applications

In this chapter, we have discussed the synthesis of 5-chloro-1*H*-benzotriazole and its derivatives. By using 5-chloro-1*H*-benzotriazole as a starting material, we have synthesized over sixteen fused compounds for high energy material applications. All the compounds are characterized by spectroscopic (^{1}HNMR, ^{13}CNMR, IR, MS, etc.) analysis. The Melting and decomposition temperatures were measured by thermogravimetric analyses. In addition, the energetic properties including, the heat of formation, density, detonation parameters, chemical energy of detonation were calculated by computational studies.

Among the synthesized compounds, 5-chloro-4-nitro-1*H*-benzo[1,2,3]triazole (**2.2**) and 5-azido-4,6-dinitro-1*H*-benzo[1,2,3]triazole (**2.7**) were characterized by single crystal X-Ray technique. Based on the energetic properties of all these compounds, it was predicted that they can be used as insensitive energetic materials. In this chapter, we have synthesized total sixteen molecules (Figure 1.8 and 1.9). Among the synthesized compounds, 4,6-dinitro-1*H*-benzo[1,2,3]-5-amine (**2.6**), 5-azido-4,6-dinitro-1*H*-benzo[1,2,3]triazole (**2.7**), 5-azido-4,6,7-trinitro-1*H*-benzo[1,2,3]triazole (**2.8**), 4-nitro-6*H*-[1,2,3]triazolo[4,5-e][2,1,3]benzoxadiazole-1-oxide (**2.9**), 4,6-dinitro-5-(3-nitro-1*H*-pyrazole -1-yl)-1*H*-benzo[d][1,2,3]triazole(**2.11**),4,6-dinitro-5-(3-nitro-1*H*-1,2,4-triazol-1-yl)-1*H*-benzo[d][1,2,3]triazole (**2.12**) show the combination of reasonable performance and thermal stability. Thus, on the basis of calculated energetic properties, it is predicted that they can be used as insensitive energetic materials in various high energy material field [25].



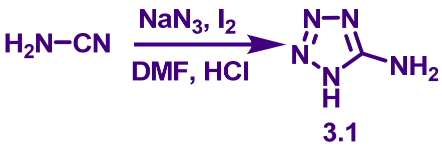
Scheme 1.1: Synthesis of amino, azido, and nitro derivatives of 1H-benzo [1,2,3]triazole.



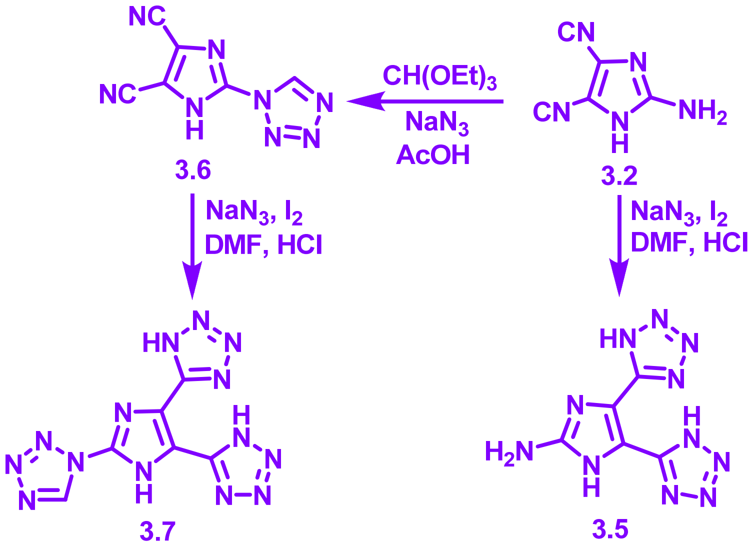
Scheme 1.2: *Catalytic N-arylation of substituted azoles with 5-chloro-4,6-dinitro-1H-benzo[1,2,3]triazole (3) using CuI (a. 4-nitroimidazole; b. 4-nitropyrazole; c. 3-nitro-1,2,4-triazole; d. 1H-tetrazole; e. 2-amino-1H-tetrazole; f. 3-trifluoromethyl-1H-pyrazole; and g. 3,5-bis(trifluoromethyl)-1H-pyrazole).*

Chapter 3: Synthesis of nitrogen-rich imidazole, 1,2,4-triazole and tetrazole-based compounds

Five member nitrogen containing rings such as imidazole, pyrazole, triazole and tetrazole are the natural framework for energetic materials as possesses high nitrogen content [26]. Among these heterocyclic compounds, tetrazole is a powerful building block for high energy density materials (HEDMs) due to its high nitrogen content (~80%), high positive heat of formation (320 kJmol^{-1}), low sensitivity towards impact and good thermal stability due to its aromatic ring system. This allows substitution of various energetic groups or designing of compounds with varying performance and sensitivity. Due to its significant energetic properties, a variety of tetrazole-based energetic compounds have already been synthesized. Moreover, introduction of nitro, azido or azo groups, salt formation and N-oxidation in tetrazole have been developed to improve the properties of tetrazole based energetic materials. Due to high nitrogen content and consequently high average two electron bond energy associated with the N–N triple bond formation, these compounds have variety of applications as low-smoke producing pyrotechnic compositions, [27] gas generators, [28] propellants [29] and high explosives [30]. Gas generators are used to generate large amount of gas, as for turbopumps, to inflate balloons, especially airbags, to eject parachutes and for similar applications.



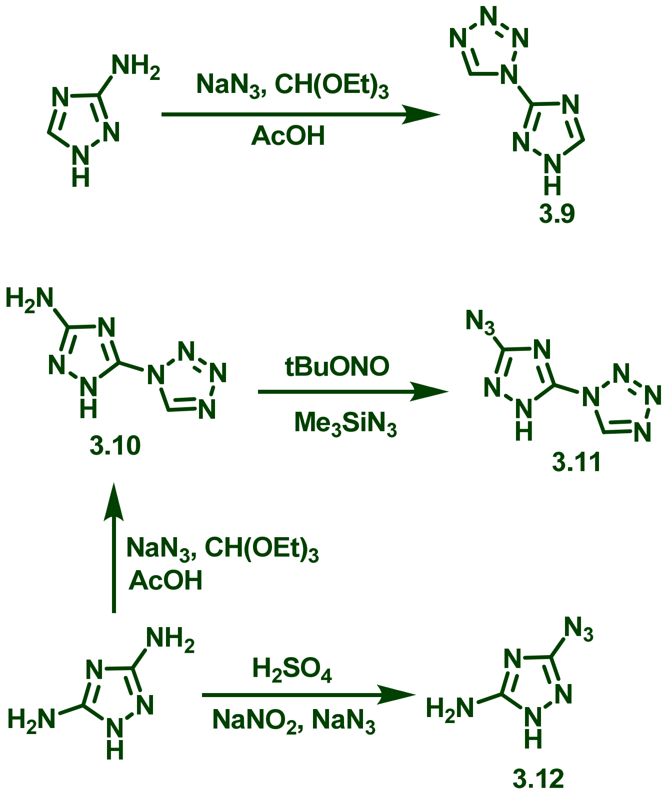
Scheme 1.3. Synthesis of 5-aminotetrazole.



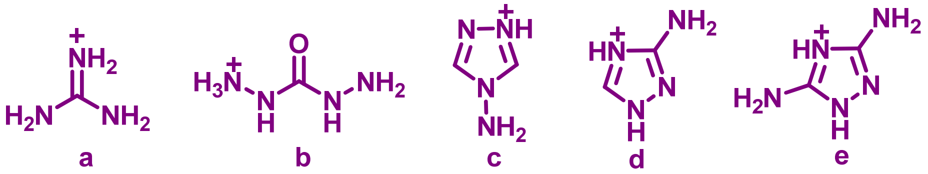
Scheme 1.4: Synthesis of imidazole derivatives.

In this chpter, we have described the synthesis of energetic salts based on the 1-(1*H*-1,2,4-triazol-3-yl)-1H-tetrazole (**3.9**), 5-(1*H*-tetrazol-1-yl)1*H*-1,2,4-triazol-3-amine (**3.10**), 1-(3-azido-1*H*-1,2,4-triazol-5-yl)1*H*-tetrazole (**3.11**) and 3-azido-1*H*-1,2,4-triazol-5-amine (**3.12**) anions. The presence of high nitrogen content and higher enthalpy of formation of molecules containing 1,2,3-triazoles and tetrazoles in their molecular structure would enable their use as high enthalpy modifiers in energetic materials. All compounds were characterized by means of elemental analysis, mass spectrometry (MS), IR and NMR (^{1}H and ^{13}C) spectroscopy. The densities of most of the salts range from 1.55 to 1.78 g cm^{-3}. The calculated detonation pressures

(*DP*) were in the range 14.7–27.2 GPa, and detonation velocity (*VOD*) were in between 6.0 and 7.85 kms^{-1}, which are more or less close to that of trinitrotoluene (TNT) (P = 19.5 GPa, D = 6.8 kms^{-1}) [31].



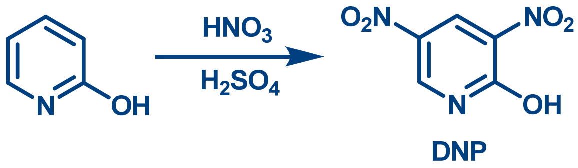
Scheme 1.5: Synthesis of nitrogen-rich triazole-tetrazole based compounds.



Scheme 1.6. Selected nitrogen-rich cationic moieties for salt preparation.

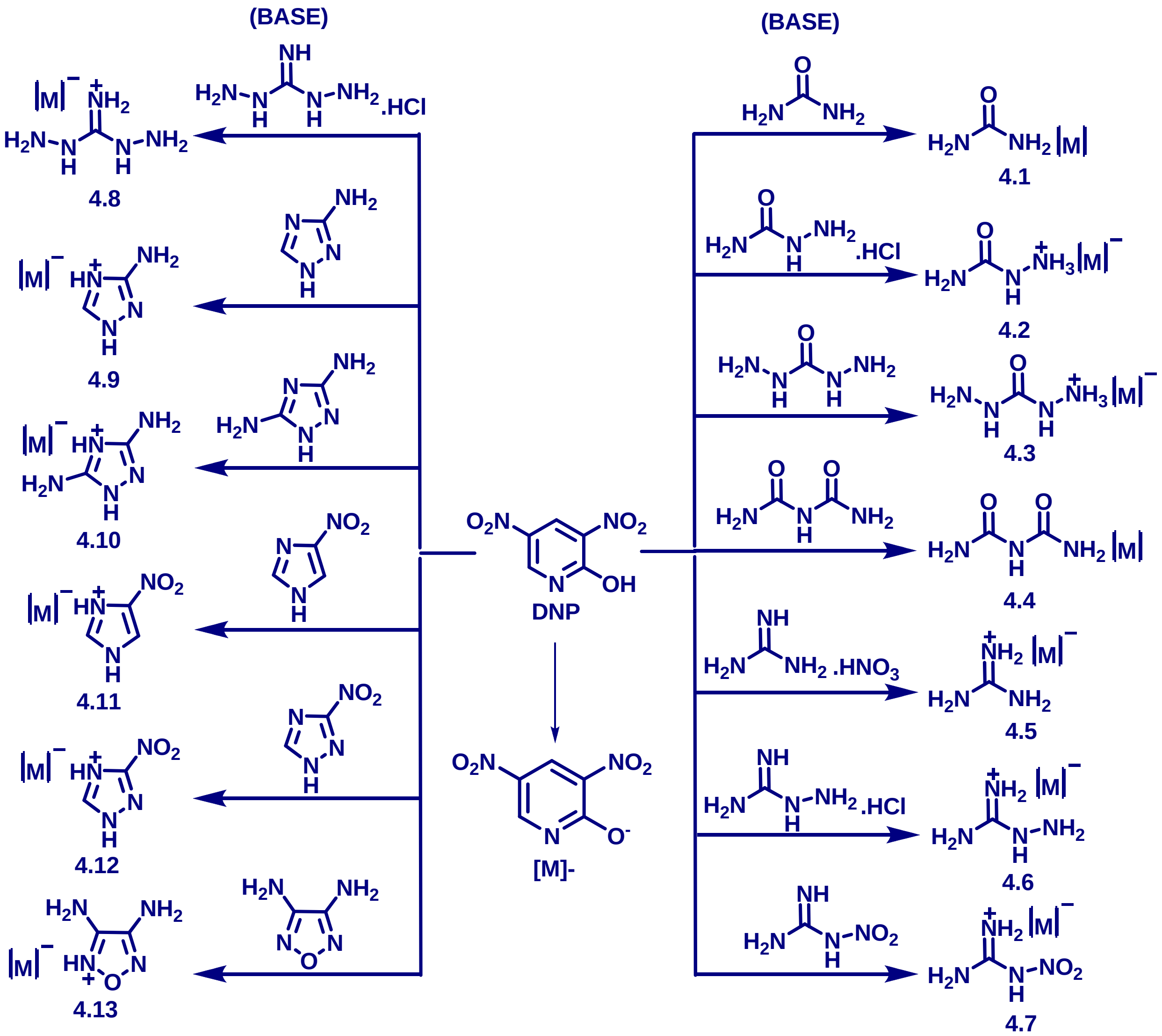
Chapter 4: Energetic Monoanionic Salts of 3,5-Dinitropyridin-2-ol

The potential of pyridine derivatives in generating energetic materials with good performance and reasonable thermal stability has been reported [32]. However, pyridine-based salts have not been explored for their possible application as energetic materials. This prompted us to investigate the potential of the neutral 3,5-dinitropyridin-2-ol (DNP) as possible precursor for the synthesis of ionic salts.



Scheme 1.7: Synthesis of 3,5-dinitropyridin-2-ol.

Consequently, we have described the preparation of energetic salts based on a DNP anion in combination with urea, semicarbazide, carbohydrazide, biuret, guanidine, aminoguanidine, nitroguanidine, 1,3-diaminoguanidine, 3-amino1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 4-nitroimidazole, 3-nitro-1,2,4-triazole and 3,4-diaminofurazan as cations (Figure 1.15). We have fully characterized 3,5-dinitropyridin-2-ol and its thirteen monoanionic salts (**4.1–4.13**) by ^{1}H, ^{13}C NMR, and IR spectroscopy, as well as thermogravimetric differential thermal analyses, mass spectroscopy, and elemental analyses. Favorable structure–property relationships were achieved by changing the cationic moieties. The densities of the DNP salts range between 1.60–1.74 g cm^{-3}, whereas detonation velocities and pressures were calculated to be in the range 6.51–7.56 kms^{-1} and 17.57–24.84 GPa respectively. Based on contributions to the energetic properties, the most promising cation for use in energetic DNP salts of those studied were nitroguanidine and 3-nitro-1,2,4-triazole.



Scheme 1.8: Synthesis of 3,5-dinitropyridin-2-ol salts.

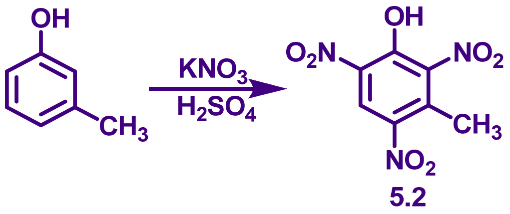
Base is one of the imidazole, tetrazole or guanidinium derivatives shown on the top of every arrow

Chapter 5: Energetic salts prepared from Phenolate derivatives

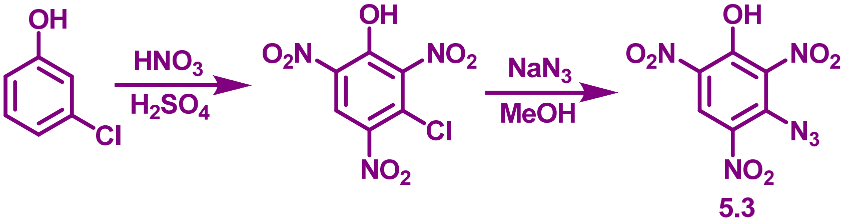
The chemistry of polynitroarenes have been widely studied and used in civil as well as military applications due to their remarkable properties [33]. Benzene compounds having three or more nitro groups, exhibit distinctly marked explosive properties (e.g. 2-methyl-1,3,5-trinitrobenzene (TNT), 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitroaniline (picramide) 2,4,6-trinitroanisole, 1,3-diammino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-

trinitrobenzene (TATB), etc.). Nitro group is an important source of oxygen in nitroarenes and most of these compound release energy mainly from the oxidation of hydrocarbon backbone. Thus, the combination of these compounds with heterocyclic compounds were expected to modify energetic properties. Previously, few salts of phenolate have been reported [34]. Salts of picric acid with ammonium, guanadinium, or heavy metal cations represented promising properties for applications in military charges and in initiating mixtures [35]. Nitrophenols have limited applications in energetic materials as they are known to react with surrounding metals to yield very sensitive compounds. Nitrophenols are also well known for salt formation and to stabilize the materials through the formation of hydrogen-bonded networks [36].

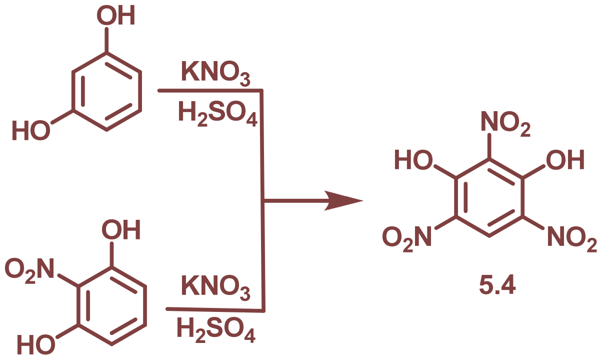
We have synthesized energetic salts based on picric acid (**5.1**), 2,4,6-trinitro-m-cresol (**5.2**), 3-azido-2,4,6-trinitrophenol (**5.3**), styphnic acid (2,4,6-trinitrobenzene-1,3-diol) (**5.4**) and 2,4,6-trinitro-1,3,5-benzenetriol (**5.5**) with concomitant determination of structural and thermal properties. In addition, we have extended our studies to understand structure-performance relationship with various cations in combination with phenolate anions having 1:1, 2:1 and 3:1 charge ratio. While the typical cations used in these systems are for example, 4-amino-4*H*-1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 3,4-diaminofurazan and guanidine. Their structures were characterized and confirmed by ^{1}H, ^{13}C NMR, DEPT spectroscopy, IR spectroscopy, MS and elemental analysis. The calculated detonation pressures of picric acid salts (**5.1a-5.1e**), styphnic acid (**5.4b-5.4e**) and 2,4,6-trinitrophloroglucinol (**5.5a-5.5e**) lie in the range between P=16.8 and P=24 GPa and detonation velocities lie between D=6.4 and D=8 km/s. Comparing the performance characteristics of 2,4,6-trinitro-m-cresol (**5.2a-5.2e**) and 3-azido-2,4,6-trinitrophenol (**5.3b-5.3e**) salts reveals that 3-azido-2,4,6-trinitrophenol salts possess better performance due to their high densities. Comparing energetic properties of picric acid, styphnic acid and 2,4,6-trinitro-1,3,5-benzenetriol reveals that –OH group tends to reduce heat of formation, while improving density, oxygen balance and thus, performance. In summary, all the phenolate salts exhibit good thermal stabilities, better densities, reasonable detonation pressures and detonation velocities.



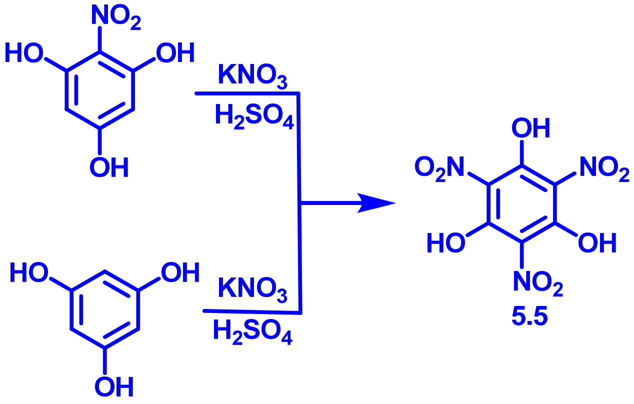
Scheme 1.9: *Synthesis of 2,4,6-trinitro-m-cresol.*



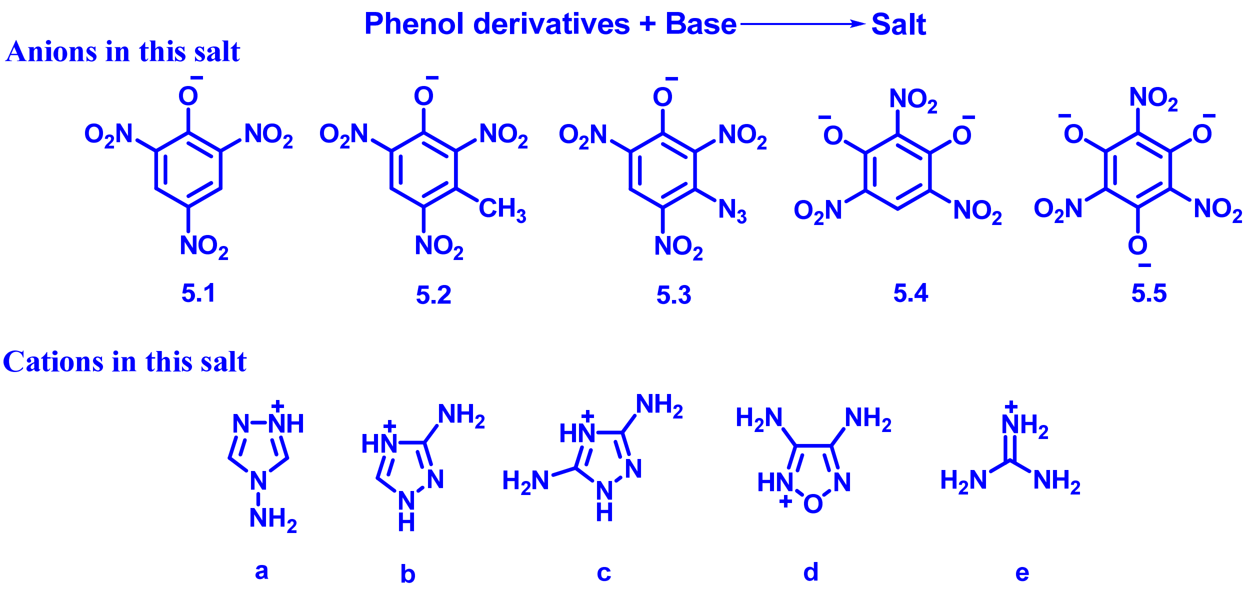
Scheme 1.10: *Synthesis of 3-azido-2,4,6-trinitrophenol.*



Scheme 1.11: *Synthesis of styphnic acid.*



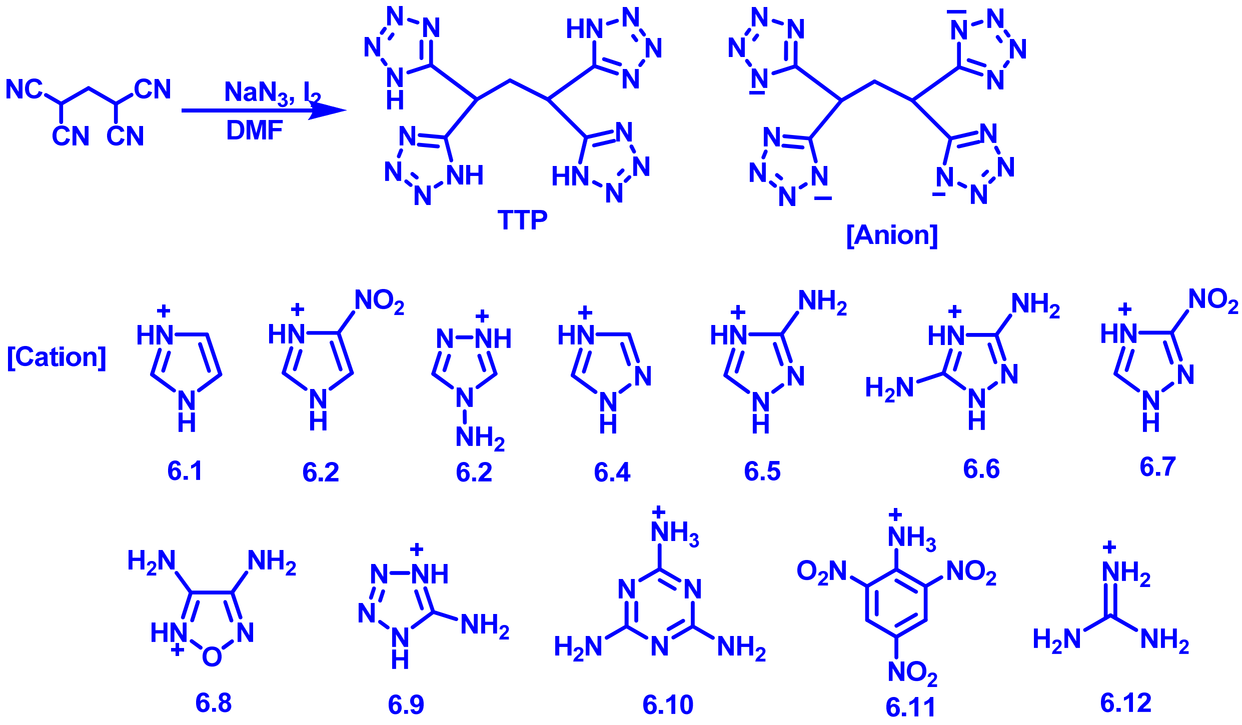
Scheme 1.12: *Synthesis of 2,4,6-trinitrophloroglucinol.*



Scheme 1.13. Synthesis of energetic salts from nitrophenolate derivatives.

Chapter 6: Tetraanionic Nitrogen-Rich Based Energetic Salts Tetrazole

In this chapter, we report the synthesis, characterization, and energetic properties of nitrogen-rich 1:4 of energetic tetra anionic 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane (TTP) and their various salts. In the energetic materials, there are no reportes available on salts with 1:4 ratio of cation and anion. We have successfully synthesized all the salts by simple and straight forward manner using methanol as solvent. All the compounds were characterized by spectroscopic studies (NMR, IR, MASS, HRMS) and the percentage of nitrogen, oxygen were calculated by elemental analyses. The thermal stabilities of these compounds were studied through the thermogravimetric analyses. The energetic properties of the synthesized molecules were examined with respect to the individual constituent atoms present in the molecules. All the molecules are showing excellent nitrogen percentage in their back bone. Because of its high nitrogen percentage these materials can be used as a high energetic materials, gas generators and solid rocket propellants. All the molecules are decomposing more the 250 °C, while decomposing these materials will release high amount of nitrogen and can be considered in environmentally friendly applications. 1,1,3,3-Tetra(1*H*-tetrazol-5-yl)propane (**TTP**), 3-nitro-1*H*-1,2,4-triazol-4-ium5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide, 5-amino-1*H*-tetrazol-2-ium5,5',5",5"'-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide, 2,4,6-trinitrobenzenaminium-5,5',5",5"'-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide molecules possess better energetic properties and high enthalpies of formation. Overall study reveals that these materials can be used in thermally stable high energetic material, gas generators and propellant applications [37].



Scheme 1.14. Syntheses of TTP and their energetic salts.

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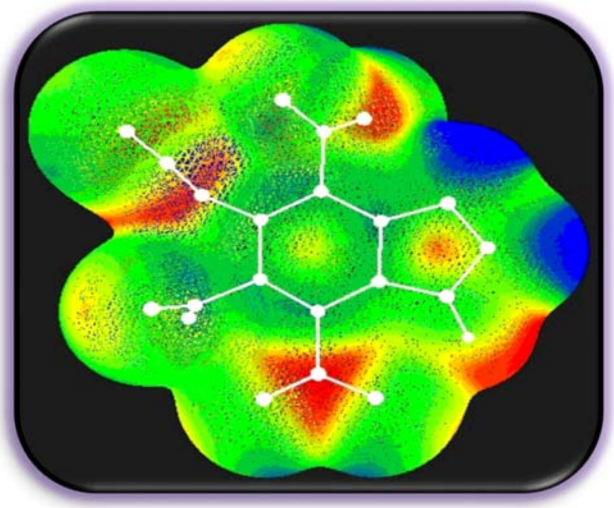
CHAPTER 2

Synthesis of Amino, Azido, Nitro and Nitrogen-rich Azole Substituted Derivatives of 1*H*-Benzotriazole

Abstract

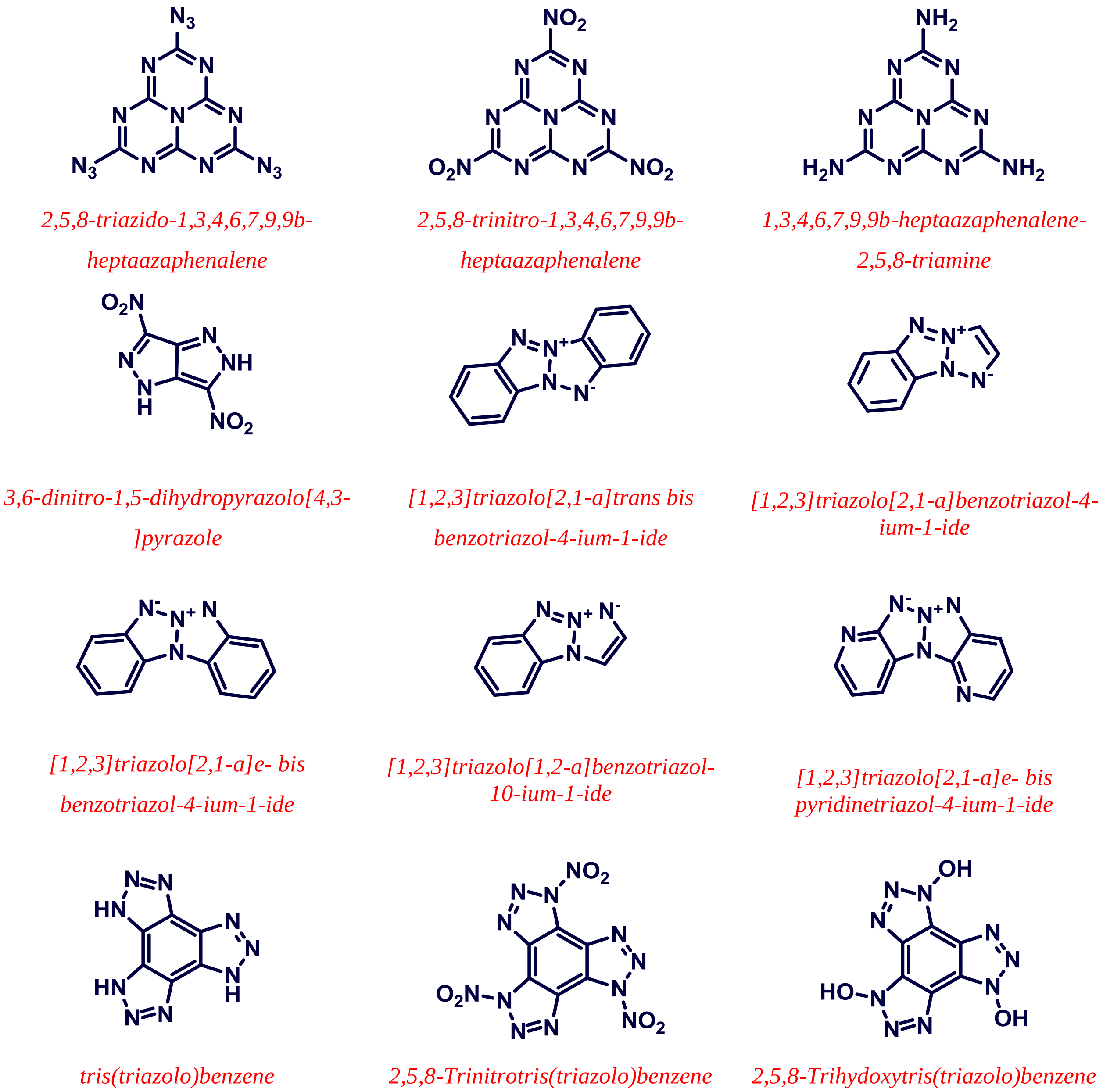
The amino, azido, nitro, and nitrogen-rich azole substituted derivatives of 1*H*-benzotriazole have been synthesized for energetic material applications. The synthesized compounds were fully characterized by ^{1}H and ^{13}C NMR, IR, Mass spectrometry and C, H, N analysis. 5-Chloro-4-nitro-1*H*-benzo[1,2,3]triazole (**5.2**) and 5-azido-4,6-dinitro-1*H*-benzo[1,2,3]triazole (**5.7**) crystallize in the $Pca2_1$ (orthorhombic) and $P2_1/c$ (monoclinic) space group, respectively as determined by single-crystal X-ray diffraction. Their densities are 1.71 and 1.77 g cm^{-3}, respectively. The calculated densities of the other compounds range between 1.61 and 1.98 g cm^{-3}. The detonation velocity (*VOD*) values calculated for these synthesized compounds range from 5.45 to 8.06 km/s, and the detonation pressure (*DP*) range from 12.35 to 28 GPa.



2.1. Introduction

The design, synthesis and characterization of energetic materials have been the interest of many researchers on the globe over the last several years [1]. As discussed in the chapter 1, there are several criteria that new high-energy materials (HEMs) should satisfy [2] to be considered as feasible replacements for currently benchmark energetic materials, such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), 2-methyl-1,3,5-trinitrobenzene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), or [3-nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate (PETN). In general, new materials should have high detonation performance comparable to those widely used high explosives in combination with good thermal stability and insensitivity towards shock and friction.

Fused heterocyclic compounds with reduced vulnerability, low shock and impact sensitivities and increased detonation performance can form a library of compounds for performance evaluation [3]. There have been many attempts to synthesize compounds with a large content of nitrogen and low (or zero) content of hydrogen in recent years due to the formation of very stable N_2 as an ultimate decomposition product. These studies reveal that high detonation velocity, reduced vulnerability, low shock and impact sensitivities over those in current use are highly desirable for synthesizing more powerful energetic compounds and can be obtained from the fused heterocycles. As a consequence, the nitrogen-rich fused rings have been widely synthesized and theoretically studied for their energetic performance. Fused rings such as pyrazolo-pyrazole [4], tetraazacyclooctatetraene (TACOT) [5], benzofuroxans [6] and s-heptazine [7], have been synthesized. In recent years, 1,3,5-triazine (s-triazine) based carbon nitride (CN_x) materials have been investigated by various researchers. The s-heptazine structure was first postulated by Pauling and Sturdivant as a component of the polymer melon $[-C_6H_7(NH_2)-NH-]_n$. s-Heptazine is symmetrical heterocyclic azadienes, composed of three fused s-triazine rings [7]. Such s-triazine monocyclic systems have been subjected to theoretical and experimental studies.



2,5,8-triazido-1,3,4,6,7,9,9b-heptaazaphenalene

2,5,8-trinitro-1,3,4,6,7,9,9b-heptaazaphenalene

1,3,4,6,7,9,9b-heptaazaphenalene-2,5,8-triamine

3,6-dinitro-1,5-dihydropyrazolo[4,3-]pyrazole

[1,2,3]triazolo[2,1-a]trans bis benzotriazol-4-ium-1-ide

[1,2,3]triazolo[2,1-a]benzotriazol-4-ium-1-ide

[1,2,3]triazolo[2,1-a]e- bis benzotriazol-4-ium-1-ide

[1,2,3]triazolo[1,2-a]benzotriazol-10-ium-1-ide

[1,2,3]triazolo[2,1-a]e- bis pyridinetriazol-4-ium-1-ide

tris(triazolo)benzene

2,5,8-Trinitrotris(triazolo)benzene

2,5,8-Trihydoxytris(triazolo)benzene

Figure 2.1 *Various fused ring systems used in the design and synthesis of energetic materials.*

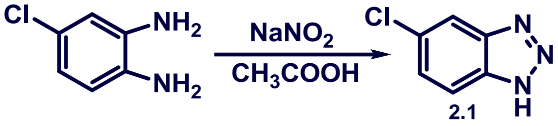
In this work, we mainly focused on benzotriazole based high energy materials with respect to the continuous interest in high energy materials (HEMs) as ingredients for propellants and explosives. Benzotriazole is a well-known fused heterocycle and is thermally stable due to its aromatic system. Espesiall, comparing with 1,2,3-triazole, the benzotriazole is more stable. The various types of benzotriazoles are significant compounds because of their wide use in organic, polymer and pharmaceutical chemistry. Especially 1*H*-benzotriazole exhibits a broad spectrum of pharmacological activity. Benzotriazolyl groups have been used extensively as synthetic auxiliaries for the last two decades [8]. Their advantage frequently lies in enabling rather common transformations to be formed efficiently, quickly and inexpensively [9].

Conventional energetic materials provide energy not only by breaking C-C bonds, but also through the formation of C=O bonds (CO_2). However, nitrogen-rich compounds which contain a large number of N-N and C-N bonds derive most of their energy due to N_2 formation during combustion. To make use of this phenomenon, many attempts were made to synthesize compounds with a large [10] content of nitrogen [3, 11, 13, 14]. Five member nitrogen containing rings such as imidazole, pyrazole, triazole and tetrazole are the natural framework for energetic materials as they possesses high nitrogen content [11]. Different explosophores (nitro, azido, nitrate ester, etc.) were incorporated in their molecular backbone to improve their energetic performance. Incorporation of azole rings in to a compound is also a known strategy for increasing thermal stability. Introducing (different type of nitro and floro group azoles) imidazole, pyrazole, triazole and tetrazole moieties on to the benzotriazole, substituted moietyes are giving good nitrogen content and better oxygen balance. Adding these functionolities to the ring typically alerts the heat of formation making the more possitive which is a desired charactaristic for most energitic material. The present study aimed to synthesize amino, azido, nitro and nitrogen-rich azole substituted derivatives of benzotriazole and their performance evaluation using density functional theory (DFT).

2.2. Results and discussion

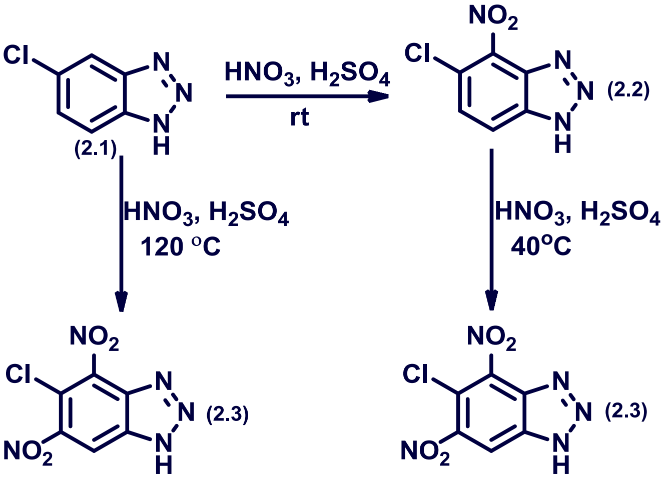
2.2.1. Synthesis and characterization

For 1*H*-benzotriazole no energetic properties were observable, but it possesses a relatively high exothermic decomposition energy of 380 $calg^{-1}$ and insensitivity to drop weight impact [12]. Nevertheless, an endothermic melting at 100 ˚C ensures safe handling at lower temperatures. At the same time, when an electronegative atom was attached to the benzotriazole nitrogen, the stability of the derived compound decreases. Consequently, the widely used 1-hydroxybenzotriazole was reported to be unstable [13]. Hence, in order to synthesize stable derivatives of 1*H*-benzotriazole we have selected 5-chloro-1*H*-benzo[1,2,3]triazole (**2.1**) as starting material and replaced chlorine by energetic groups without disturbing NH proton.



Scheme 2.1 *Synthesis of 5-chloro-1H-benzo[12,3]triazole.*

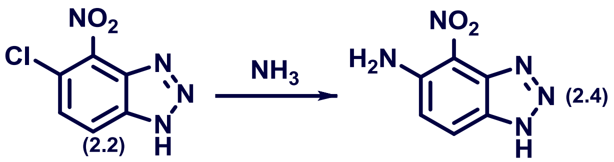
Pereira and co-workers [14] reported a simple and straight forward synthetic route for 5-chloro-1*H*-benzo[1,2,3]triazole. We have used same method to yield 5-chloro-1*H*-benzo[1,2,3]triazole, which was used for further syntheses. Stepwise reactions were performed to synthesize amino, azido, and nitro derivatives of 5-chloro-1*H*-benzo[1,2,3]triazole. The synthetic approach for nitro derivatives of benzo[1,2,3]triazole involves fuming HNO_3 and conc. H_2SO_4. Different conditions were used to synthesize of various nitrated products. In these nitrations, the reaction temperature was playing main role. Depending upon temperature, different nitration products were obtained from 5-chloro-1*H*-benzo[1,2,3]triazole. Interestingly, mononitration occurred at room temperature while dinitration occurred at temperature at 120 ° C. However, both reactions were complete within six hours.



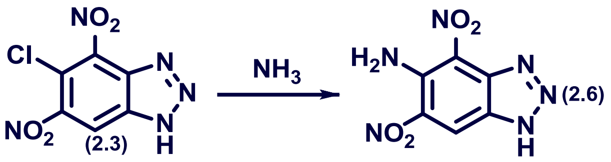
Scheme 2.2 *Synthesis of 5-chloro-4-nitro and 4,6-dinitro-1H-benzo[d][1,2,3]triazole.*

The amination reactions were carried out by treating 5-chloro-4-nitro-1*H*-benzo[d][1,2,3]triazole and 5-chloro-4,6-dinitro-1*H*-benzo[d][1,2,3]triazole derivatives with aqueous ammonia in methanol. Aqueous ammonia solution was gradually added into the reaction mixture and reflexed for three hours. In these reactions both 5-chloro-4-nitro-1*H*-

benzo[d][1,2,3]triazole and 5-chloro-4,6-dinitro-1*H*-benzo[d][1,2,3]triazole were converted to 4-nitro-1*H*-benzo[1,2,3]-5-amine (**2.4**) and 4,6-Dinitro-1*H*-benzo[1,2,3]-5-amine (**2.6**) respectively in good yields (Schemes 2.3 and 2.4).

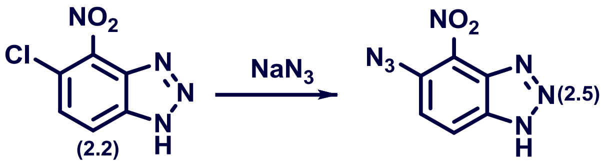


*Scheme 2.3 Synthesis of 4-Nitro-1H-benzo[1,2,3]-5-amine (**2.3**)*

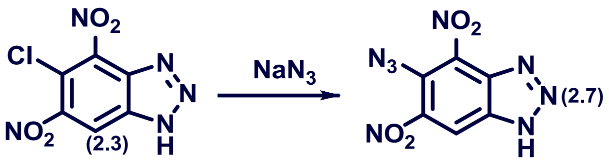


*Scheme 2.4 Synthesis of 4,6-Dinitro-1H-benzo[1,2,3]-5-amine (**2.6**)*

While doing the azidation reaction no difficulties were found. These reactions were carried out by treating 5-chloro-4-nitro-1*H*-benzo[d][1,2,3]triazole and 5-chloro-4,6-dinitro-1*H*-benzo[d][1,2,3]triazole derivatives with sodium azide in methanol. Sodium azide was gradually added into the reaction mixture at room temperature and then reflexed. The solvent was removed under reduced pressure, residue extracted with dichloromethane and purified. Both 5-azido-4-nitro-1*H*-benzo[1,2,3]triazole and 5-azido-4,6-dinitro-1*H*-benzo[1,2,3]triazole compounds were obtained with good yields.

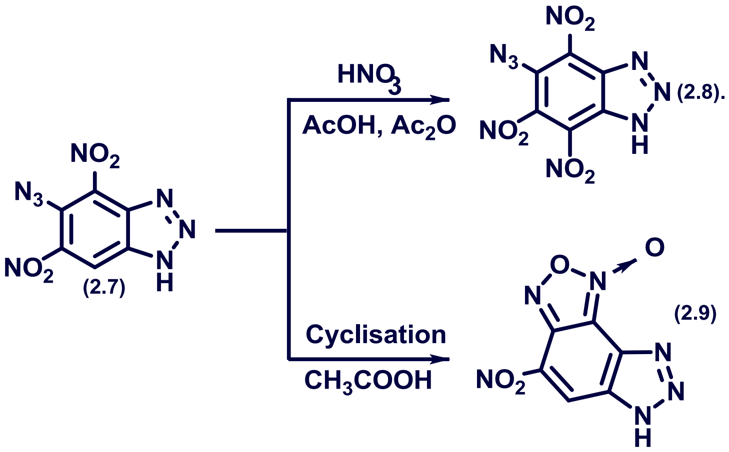


Scheme 2.5 Synthesis of Azido-4-nitro-1H-benzo[1,2,3]triazole



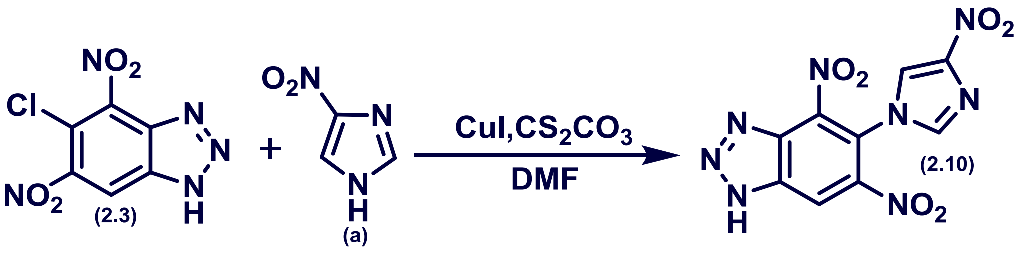
Scheme 2.6 Synthesis of 5-Azido-4,6-dinitro-1H-benzo[1,2,3]triazole

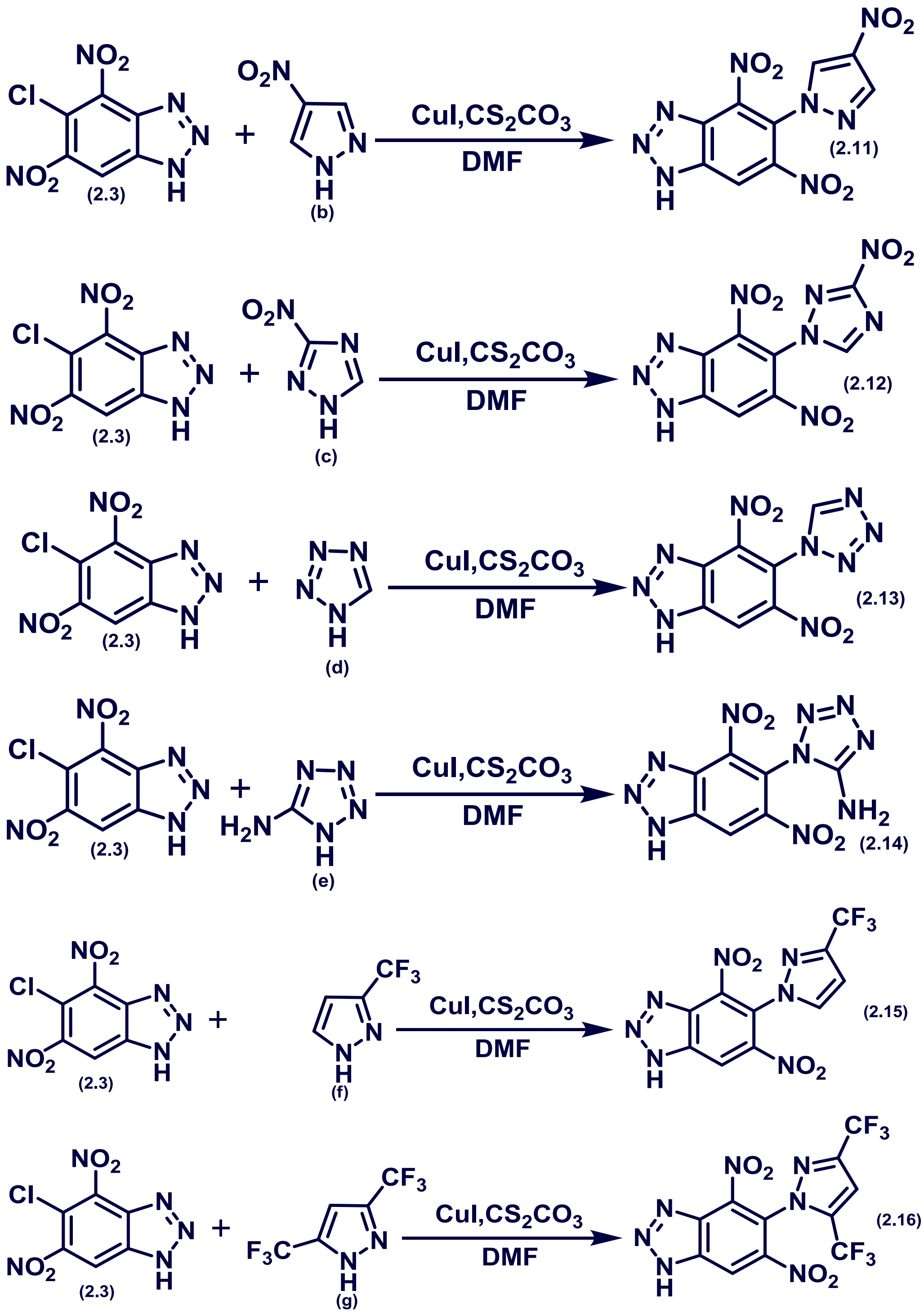
The furoxan ring formation was performed with the procedure reported in the literature by simple cyclization in the presence of acetic acid [15]. This product was obtained in good yield and characterized by NMR and mass spectral data.



Scheme 2.7 *Synthesis of 5-Azido-4,6-dinitro-1H-benzo[1,2,3]triazole and 4-Nitro-6H-[1,2,3]triazolo[4,5-e][2,1,3]benzoxadiazole-1-oxide*

Zhu et al. explored CuI-catalyzed N-arylation procedures for nitrogen containing heterocycles with aryl and heteroaryl halides [16]. The coupling reactions of substituted azoles and 5-chloro-4,6-dinitro-1*H*-benzo[1,2,3]triazole have been carried out in the presence of 20 mol % of CuI and 2 equivalents of Cs_2CO_3 in DMF at 120 °C under N_2 (**Scheme 2.8**). These reactions proceeded without any complications because of the presence of two nitro groups adjacent to the chlorine in 5-chloro-4,6-dinitro-1*H*-benzo[1,2,3]triazole molecule. Nitro groups of strong electron withdrawing nature could pull the electrons so that the carbon chlorine bond became week. The method developed here for the synthesis of energetically useful compounds, involves simple chemistry and is practicable in any laboratory. Moreover, the method did not require any complicated, sensitive and costly reagents for nitration reactions. The compounds were also derived from simple, readily available starting materials.





Scheme 2.8 Catalytic N-arylation of substituted azoles with 5-chloro-4,6-dinitro-1*H*-benzo[1,2,3]triazole (**2.3**) using CuI (**a**. 4-nitroimidazole; **b**. 4-nitropyrazole; **c**. 3-nitro-1,2,4-triazole; **d**. 1*H*-tetrazole; **e**. 2-amino-1*H*-tetrazole; **f**. 3-trifluoromethyl-1*H*-pyrazole; and **g**. 3,5-bis(trifluoromethyl)-1*H*-pyrazole)

The structures of all the products were confirmed by IR, ^{1}H, ^{13}C NMR and DEPT spectra and mass spectral date. ^{1}H and ^{13}C NMR spectra of compounds 2.1 to 2.16 are included at the end of this chapter (Figure 2.S1 - 2.S34). The spectral data were consistent with the expected structures of the molecules. The compounds **2.2** and **2.7** were further confirmed by single crystal X-ray crystallography. The structures of compounds **2.2** and **2.7** were solved by direct method and refined on F^2 by full-matrix least-squares procedures. All non- hydrogen atoms were refined anisotropically. Crystallographic data and packing for compound **2.2** and **2.7** are summarized in Table 2.1. Selected bond lengths and bond angles for compound **2.2** and **2.7** are listed in figure **2.1** and **2.2.** The packing of compounds **2.2** and **2.7** is also characterized by a three-dimensional network; those images are showed in figure 2.3 and 2.4.

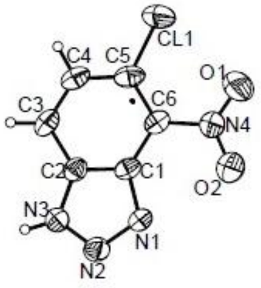


Figure 2.2. *ORTEP of the molecular structure of* **2.2**. Thermal ellipsoids are shown at 30% probability levels. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles[°]:N1–N2=1.351(8),N3-N4=1.297(8),N3-C2=1.376(8),C2-C3=1.434(9),C3C4=1.363(10), C5-C4=1.407(10),C5-C11=1.718(7), C5-C6=1.391(8), N4-C6=1.446(9), C1-C6=1.413(8), C2-C1=1.358(9), N1-C1=1.370(7), N4-O2=1.199(8),N4-O1=1.200(8), C5-C6-C1=115.8(6), C5-C6-N4=125.0(6), C1-C6-N4=119.1(5), C6-C5-C4=120..5(6), C6-C5-C11=119.9(5), C2-C1-N1=104.4(5), C2-C1-C6=122.6(5), N1-C1-C6=132.9(6), N2-N1-C1=109.1(5), O2-N4-O1=121.8(7), O2-N4-C6=115.6(6), O1-N4-C6=122.5(6), N3-N2=-C2=107.1(5), C4-C3-C2=114.4(6), N3-N2-N1=109.6(5), C1-C2-N3=109.7(5), C1-C2-C3=122.2(6), N3-C2-C3=128.0(6), C3-C4-C5=124.3(6).

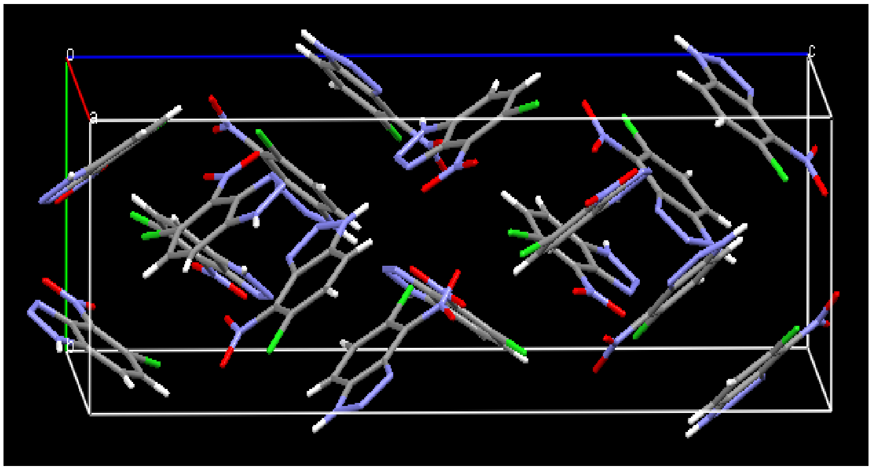


Figure 2.3. *Crystal packing diagram for compound* **2.2**.

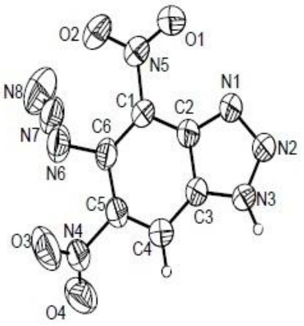


Figure 2.4. *ORTEP of the molecular structure of* ***2.7****.* Thermal ellipsoids are shown at 30% probability levels. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles[°]:N1-N2=1.338(3), N1-C2=1.344(3), N3-N2=1.286(3), N3-C3=1.365(4), C2-C3=1.387(4), C2-C1=1.402(4), C3-C4=1.380(4), N5-O2=1.210(3), N5-O1=1.215(3), N5-C1=1.445(4), C1-C6=1.396(4), N4-O3=1.192(4), N4-O4=1.187(3), N4-C5=1.472(4), C5-C4=1.367(4), C5-C6=1.415(5), C6-N6=1.412(4), N6-N7=1.226(5), N7-N8=1.128(5), N2-N1-C2=110.3(2), N2-N3-C3=109.4(2), N1-C2-C3=104.8(2), N1-C2-C1=134.0(3), C3-C2-C1=121.2(2), N3-C3-C4=130.9(3), N3-C3-C2=107.0(2), C4-C3-C2=122.1(3), O2-N5-O1=123.1(3), O1-N5-C1=117.5(2), C6-C1-C2=118.1(3), C6-C1-N5=124.1(3), C2-C1-N5=117.8(3).

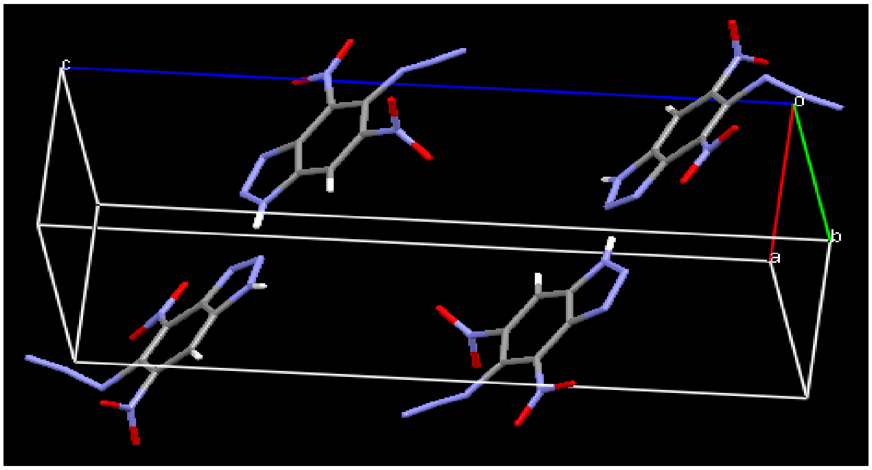


Figure 2.5 *Crystal packing diagram for compound* ***2.7****.*

Table 2.1. *Crystal data and structural refinement details for **2.2** and **2.7**.*

Parameters	**2.2**	**2.7**
Empirical formula	$C_6H_3N_4O_2Cl$	$C_6H_2N_8O_4$
Formula weight	198.57	250.13
Crystal System	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/c$
a (Å)	15.5042(12)	5.7213(14)
b (Å)	7.9764(8)	8.814(2)
c (Å)	24.9015(19)	18.596(4)
α (deg)	90.00	90.00
β (deg)	90.00	91.55(4)
γ (deg)	90.00	90.00
Volume $(Å)^3$	3079.5(5)	937.4(4)
Temperature (K)	293(2)	293(2)
Z	16	4
μ mm^{-1}	0.464	0.152
D (calcd.) (gcm^{-3})	1.713	1.773
F(000)	1600	504
θ range (deg)	2.75-28.98	2.19-24.94
Index ranges	$-18 \leq h \leq 15$	$-6 \leq h \leq 6$
	$-9 \leq k \leq 5$	$-10 \leq k \leq 10$
	$-29 \leq l \leq 17$	$-22 \leq l \leq 21$
Collected	7838	8519
Data completeness	98.9%	99.8%
Parameters	469	163
Goodness-of-fit on F^2	1.031	1.013
Final R indices	0.0702	0.0848
$R_1 = \sum \lVert F_o - F_c \rVert / \sum \lvert F_o \rvert$	0.0562	0.0615
$wR_2 = [\sum(F^2_o - F^2_c)/\sum w(F_o)^2]^{1/2}$	0.1505	0.1639

2.2.2. Energetic properties

The energetic properties data of the selected compounds are listed in Table 2.2. When compared with compound **2.4,** it appears that introduction of additional nitro group in **2.6** improves the oxygen balance and density and hence, the performance. A similar trend is observed for compounds **2.5, 2.7** and **2.8**. Oxygen balance (OB) is the percentage of oxygen chemically bound in a molecule to oxidize it completely. The sensitivity, strength and stability of an explosive are all to some extent dependent upon the oxygen balance. Although all of the described compounds in this study have negative OB values, most of them have better oxygen balance than TNT (-74%). Compound **2.8** exhibits the least negative oxygen balance of -35.3%.

The enthalpy of formation is one of the most important parameters to be considered in the design of energetic materials. Compounds **2.4** to **2.14** have positive heats of formation; however **2.15** and **2.16** have shown negative heats of formation. The highest positive heat of formation in the series is exhibited by compounds **2.13** and **2.14** as 752.86 and 717.67 kJmol^{-1}, respectively. The predicted densities for compound **2.2** (1.73 gcm^{-3}) and **2.7** (1.74 gcm^{-3}) are found close to the experimental densities as 1.71 and 1.77 gcm^{-3}, respectively obtained from X-ray crystallography analysis. The calculated densities of the other compounds range between 1.61 and 1.98 gcm^{-3}. The calculated detonation pressures (*DP*) for the benzotriazole derivatives fall in the range of 12.35 to 28.2 GPa, (comparable to the value of 19.5 GPa for TNT) and the detonation velocities (*VOD*) are distributed from 5.45 to 8.06 kms^{-1} (comparable to that for TNT, *VOD*=6.95 kms^{-1}) [17]. The compounds **2.8** and **2.11-2.13** shows *VOD* above 7.5 kms^{-1} and *DP* over 25 GPa. Overall, based upon its performance parameters shown in Table 2.2, compound **2.8** is an especially promising energetic material candidate and compounds **2.4-2.16** are all thermally stable, since they all melt at high temperatures without undergoing thermal decomposition. It is also interesting to mention that in the case of compound **2.7**, calculated density almost comparable to the experimental crystal density. We have not calculated energetic properties of the compounds **2.2** and **2.3**, because of chlorine atom in the rings. Chlorine atom containing molecules are not useful in energetic material applications due to their toxicity and harmful decomposition products.

Table 2.2. *Calculated energetic properties of benzotriazole derivatives from* ***2.4-2.16*** *in comparison to TNT.*

Compd.	**OB[a]**	**HOF $_{\text{Solid}}$[b]**	ρ [c]	**VOD [d]**	**DP [e]**	**Q[f]**	**M.P.[g]**
2.4	-111.7	198	1.61	5.70	13.42	661.81	210
2.5	-89.8	518	1.62	5.45	12.35	561.38	160
2.6	-71.4	185	1.77	6.91	20.97	751.86	180
2.7	-57.6	540	1.74 (**1.77**)[i]	6.48	18.28	548.17	150
2.8	-35.3	561	1.73	8.06	28.15	1044.94	128
2.9	-64.9	466	1.98	7.25	24.67	548.17	115
2.10	-70.0	387	1.73	7.33	23.27	980.76	132
2.11	-70.0	446	1.81	7.65	26.03	1024.21	168
2.12	-57.3	483	1.75	7.64	25.44	999.86	160
2.13	-66.4	753	1.71	7.60	24.81	1200.91	140
2.14	-65.8	718	1.68	7.43	23.48	1164.20	160
2.15	-84.0	-160	1.73	7.23	22.64	1008.55	182
2.16	-75.9	-829	1.84	6.94	21.64	738.15	178
TNT	-74.0	-69 (-63)[h]	1.68 (1.65)[j]	7.20 (6.95)[j]	22.49 (19.5)[j]	1043.79	80

[a] Oxygen balance (%). [b] Solid phase HOF (kJmol^{-1}). [c] Density (gcm^{-3}) [d] Detonation velocity. (kms^{-1}) [e] Detonation pressure (GPa). [f] Chemical energy of detonation (calg^{-1}). [g] Melting point in °C. [h] Values taken from Ref [18]. [i] Value in parenthesis obtained experimentally from X-ray diffractometer crystal analysis. [j] Values taken from Ref [17].

2.3. Summary

In summary, we have synthesized a number of amino, azido, nitro and nitrogen-rich azole substituted derivatives of 5-chloro-1*H*-benzo[1,2,3]triazole using simple, scalable methods without the need for complicated purifications. All the molecules were characterized by standard techniques. These methods allow for the easy introduction of these functionalities, which are commonly added to in energetic materials to improve their energetic performance. The energetic properties and thermal analyses of compounds **2.8-2.15** reveals comparable performance to that for TNT and confirmed the potential application of these molecules in the area of energetic materials. Further, investigations are under way in order to elucidate their role as energetic materials and analysis of their energetic properties.

2.4. Experimental section

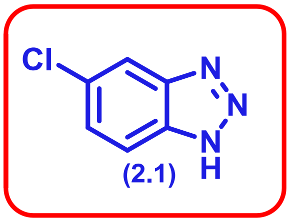
2.4.1. Materials and instrumentation

The reagents were available commercially and were used as purchased without further purification. Reactions were monitored by TLC, using pre-coated silica gel TLC plates obtained from Merck. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. The data were reported in parts per million (δ) with solvent proton as an internal standard (CD_3OD at 3.31 ppm, DMSO-d6 at 2.5 ppm and tetramethylsilane (TMS) at 0.00 ppm). Mass spectrometry was performed on LC-MS spectrometer. Elemental analysis was carried out using a Thermo Finnigan Flash EA 1112 analyzer. Melting points were determined by open capillary tubes. The IR spectra were recorded on a Perkin–Elmer IR spectrometer by using KBr pellets.

Determination of the unit cell parameters and the intensity data collection at 298 K for compound **2.2** was performed on an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer using graphite monochromated M_o K_α radiation (λ= 0.71073 Å). The CrysAlisPro software [21] was used for data collection, reduction and absorption correction. For compound **2.7**, Bruker-Nonius SMART APEX CCD single crystal diffractometer, equipped with a graphite monochromator and a M_o K_α fine-focus sealed tube (λ= 0.71073 Å) was used to determine the unit cell parameters and intensity data collection at 298 K. The SMART and the SAINT-Plus packages [19] were used for data acquisition and data extraction, respectively. The SADABS program [20] was used for absorption corrections.

2.4.2. Synthetic procedures

***Synthesis of 5-chloro-1H-benzo[1,2,3]triazole* (*2.1*):** Sodium nitrite (0.30 g, 4.34 mmol) was added at 5 °C in a solution of 4-chlorobenzene-1,2-diamine (0.29 g, 2 mmol) in acetic acid (10 mL) and sonicated in an ultrasonic water bath at 5-10 °C for 12-15 minutes. After this, the solvent was removed, the organic phase extracted with methylene dichloride, washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the products were isolated with satisfactory purity as brown powder compound (**2.1**) (0.160 g, 55% yield). Melting point 145 ˚C.



(2.1)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3107 (m), 3070 (s), 3042 (s), 2953 (m), 2771 (m), 1626 (s), 1589 (s), 1392 (s), 1307 (s), 1259 (s), 1199 (s), 1060 (s), 1018 (s), 991 (vs), 800(s).

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.030 (s, *J* 7.88Hz, 1H), 7.962 (d, *J* 8.8 Hz, 1H), 7.44.(d, 8.6 1H).

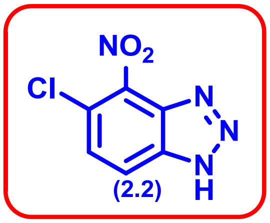
^{13}C NMR (100MHz, DMSO) : δ (ppm) 138.83, 137.95, 131.69, 126.33, 115.99, 113.51.

Mass : 153.77.

Anal. Calcd. for $C_6H_4N_3Cl$: C, 46.93; H, 2.63; N, 27.36.

Found : C, 47.05; H, 2.71; N, 27.21.

***5-Chloro-4-nitro-1H-benzo[1,2,3]triazole* (*2.2*):** 5-Chloro-1*H*-benzo[1,2,3]triazole (0.459 g, 0.003 mmol) was added to the 1:2 mixture of fuming HNO_3 and 98% H_2SO_4 in ice bath. After this, the reaction mixture was stirred for 6h at 60 ˚C and poured the reaction mixture into crushed ice. The resulting yellow solid was collected by filtration and washed with excess of water, then dried under vacuum. The crude product was recrystallized from *n*-hexane/EtOAc to give (**2**) (0.473 g, 80% yield) as white solid. Melting point 225 ˚C.


(2.2)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3073 (s), 2991 (m), 2909 (s), 2854 (s), 1747 (m), 1627 (vs), 1479 (s), 1413 (s), 1331 (vs), 1243 (vs), 1156 (s), 1084 (s), 986 (s), 816 (s), 767 (s).

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 8.293 (d, *J* =7.2, 1H), 7.711 (d, *J* =7.2 Hz, 1H).

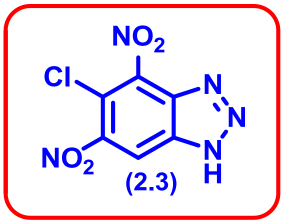
^{13}C NMR (100MHz, CD_3OD) : δ ppm 143.29, 132.80, 130.66, 127.86, 127.58, 123.02.

Mass : 198.57.

Anal. Calcd. for $C_6H_3N_4O_2Cl$: C, 36.29; H, 1.52; N, 28.22.

Found : C, 36.21; H, 1.56; N, 28.15.

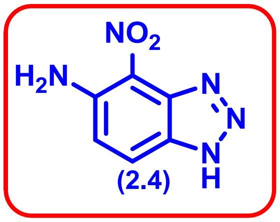
5-Chloro-4,6-dinitro-1H-benzo[1,2,3]triazole (2.3): 5-Chloro-4-nitro-1*H*-benzo[1,2,3]-triazole (0.3 g, 1.5 mmol), was added to the 1:2 mixture of fuming HNO_3 and 98% H_2SO_4 in ice bath. Then the reaction mixture stirred at for 6h 120 ˚C and poured the reaction mixture into crushed ice. The resulting crystalline solid was filtered off and washed thoroughly with water, until the pH become 7 and then dried under vacuum. The crude product was purified by column chromatography over silica gel with *n*-hexane/EtOAc to give (**2.3**) (0.400 g, 54.8% yield) as white solid. Melting Point: 198 ˚C.


(2.3)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3067 (s), 1630 (s), 1558 (vs), 1396 (s), 1334 (vs), 1224 (s), 1089 (s), 1001 (s), 945 (s), 879 (s), 815 (s), 787 (m), 696 (m), 578 (m).

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) (s, 1H), 8.987.
^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 146.36, 134.36, 131.89, 128.26, 119.72.
Mass : 243.56.
Anal. Calcd. for $C_6H_2N_5O_4Cl$: C, 29.59; H, 0.83; N, 28.75.
Found : C, 29.51; H, 0.86; N, 28.86.

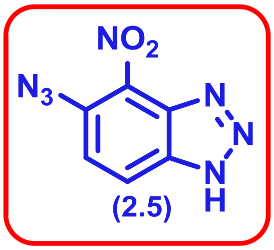
4-Nitro-1H-benzo[1,2,3]-5-amine (2.4): 5-Chloro-4-nitro-1H-benzo[1,2,3]triazole (0.3 g, 1.5 mmol) was dissolved in methanol (8 mL) and aqueous 24% NH_3 (20 mL) was gradually added. The reaction mixture stirred at ~ 20 ˚C for 2.5h, refluxed for 3h and left for ~14 hrs. The precipitate formed was filtered off and the filtrate was evaporated to dryness. The solid residue was combined with the precipitate, after this water (25 mL) and HCl (25 mL) were added. On stirring, the precipitate was filtered off and washed with water to neutral The crude product was purified by column chromatography over silica gel with *n*-hexane/EtOAc to give (**2.4**) (0.22 g, 82% yield) as yellow solid. Melting point: 210 ˚C.



(2.4)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3440 (m), 3331 (m), 3068 (s), 2958 (m), 2920 (s), 2860 (s), 1643 (s), 1621 (vs), 1539 (s), 1484 (vs), 1408 (vs), 1331 (s), 1243 (s), 1073 (s), 986 (s).
^{1}H NMR (400 MHz, CD_3OD) : δ ppm 8.263 (d, *J* 8.8, 1H), 7.745 (d, *J* 8Hz, 1H).
^{13}C NMR (100MHz, CD_3OD) : δ ppm 145.78, 140.70, 133.08, 130.14, 127.11, 118.10.
Mass : 180.
Anal. Calcd. for $C_6H_5N_5O_2$: C, 40.23; H, 2.81; N, 39.10.
Found : C, 40.31; H, 2.75; N, 39.25.

5-Azido-4-nitro-1H-benzo[1,2,3]triazole (2.5): 5-Chloro-4-nitro-1*H*-benzo[1,2,3]triaz-ole (0.3 g, 1.5 mmol) dissolved in methanol (9 mL) and sodium azide (0.117 g, 1.8 mmol) was added and the reaction continued for 2 hrs at room temperature. The resulting mixture was refluxed for additional 2 hrs. After this, the solvent was removed, the residue extracted with methylene dichloride, washed with water. The solvent was removed under reduced pressure. The crude product was purified by column chromatography over silica gel with *n*-hexane/EtOAc to give (**2.5**) (0.265 g, 86.1% yield) as brown solid. Melting point: 160 ˚C.



(2.5)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3445 (m), 2926 (vs), 2856 (s), 2143 (vs), 1637 (vs), 1541 (vs), 1412 (m), 1340 (m), 1084 (s), 954 (s).

^{1}H NMR (400 MHz, CD_3OD) : δ ppm 8.284 (d, *J* 8.8Hz, 1H), 7.712 (d, *J* 8Hz, 1H).

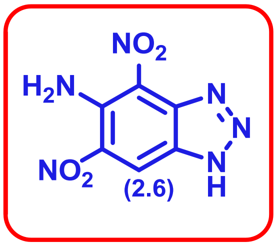
^{13}C NMR (100MHz, CD_3OD) : δ ppm 146.02, 143.03, 129.71, 127.93, 125.53, 121.22.

Mass : 204.

Anal. Calcd. for $C_6H_3N_7O_2$: C, 35.13; H, 1.47; N, 47.80.

Found : C, 35.26; H, 1.51; N, 47.68.

***4,6-Dinitro-1H-benzo[1,2,3]-5-amine* (2.6):** By a procedure identical with that described for the preparation of **2.4**, was converted into **2.6** by the reaction of 5-Chloro-4,6-dinitro-1*H*-benzo[1,2,3]triazole (0.3 g, 1.23 mmol) with aqueous 24% NH_3 (20 mL). Yellow solid compound (**2.6**) (0.235g, 87% yield). Melting point: 180 ˚C.



(2.6)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3439 (s), 3325 (s), 3059 (m), 2920 (m), 1631 (vs), 1543 (vs), 1394 (m), 1331 (vs), 1284 (vs), 1221 (vs), 1084 (m), 1001 (m), 947 (s), 881 (s), 815 (s).

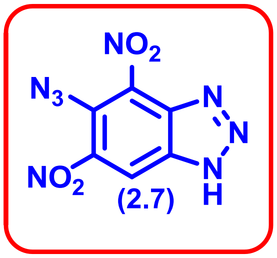
^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 9.328 (s, 1H), 4.613 (s, 2H).

^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 146.54, 141.50, 131.0, 127.92, 127.45, 118.91.

Mass : 225.

Anal. Calcd. for $C_6H_4N_6O_4$	: C, 32.15; H, 1.80; N, 37.50.
Found	: C, 32.21; H, 1.88; N, 37.45.

5-Azido-4,6-dinitro-1H-benzo[1,2,3]triazole **(*2.7*):** By a procedure identical with that described for the preparation of **2.5**, was converted into **2.7** by the reaction of 5-Chloro-4,6-dinitro-1*H*-benzo[1,2,3]triazole (0.360 g, 1.48 mmol) and sodium azide (0.115 g, 1.77 mmol). Dark brown solid compound (**2.7**) (0.140 g, 75.6% yield). Melting point: 150 ˚C.



(2.7)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3057 (m), 2924 (s), 2854 (m), 2150 (vs), 1747 (s), 1633 (s), 1541 (vs), 1396 (m), 1338 (vs), 1309 (s), 1221 (s), 1087 (s), 1012 (s), 956 (s), 796 (s), 698 (s).
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 8.203 (s, 1H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 142.09, 140.34, 129.28, 128.62, 125.10, 120.29.
Mass	: 249.
Anal. Calcd. for $C_6H_2N_8O_4$	: C, 28.81; H, 0.81; N, 44.80; O, 25.59.
Found	: C, 28.75; H, 0.93; N, 44.93; O, 25.39.

5-Azido-4,6,7-trinitro-1H-benzo[1,2,3]triazole **(*2.8*):** 5-Azido-4,6-dinitro-1H-benzo-[1,2,3]triazole (0.1 g, 4 mmol) was dissolved in acetic acid (4 mL), cooled to 0 ºC and fuming nitric acid (0.5 mL) was added slowly. After 30 min, acetic anhydride (3 mL) was added to the reaction mixture and stirring was continued for another 30 min. After this, the clear solution was poured into ice water and precipitated crude product was collected by filtration. This crude product washed with excess water and then dried under vacuum. The crude product was purified by column chromatography over silica gel with n-hexane/EtOAc to give (**2.8)** (0.5 g, 52% yield) as brown solid. Melting point:128 ˚C.


(2.8)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3445 (m), 3057 (m), 2922 (s), 2852 (m), 2148 (vs), 1626 (s), 1626 (s), 1539 (vs), 1336 (vs), 1311 (s), 1221 (s), 1087 (s), 954 (vs), 823 (s), 796 (s).

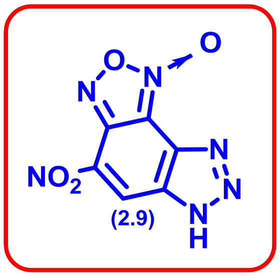
^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 146.06, 143.05, 141.13, 129.71, 125.55, 121.22.

Mass : 296.

Anal. Calcd. for $C_6HN_9O_6$: C, 24.42; H, 0.34; N, 42.71.

Found : C, 24.36; H, 0.41; N, 42.61.

***4-Nitro-6H-[1,2,3]triazolo[4,5-e][2,1,3]benzoxadiazole-1-oxide* (2.9):** Compound **2.9** was synthesized by the literature method [16]. **2.7** (0.200 g, 8 mmol) was carefully transferred into a two-necked flask fitted with a reflux condenser and acetic acid (20 ml) was added. The reaction mixture was refluxed for 2h over an oil bath; the mixture was then cooled to ambient temperature and subsequently poured into crushed ice. The precipitate thus obtained was filtered off and washed with excess distilled water to remove acid completely. The product was crystallized from methanol to give compound (**2.9**) (0.130 g 73% yield). Melting point: 115 ˚C.


(2.9)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3418 (m), 3074 (m), 2924 (vs), 2854 (s), 1716 (m), 1660 (s), 1593 (m), 1537 (s), 1439 (m), 1336 (vs), 1280 (s), 1082 (s), 987 (vs), 927 (s), 817 (s), 746 (m)

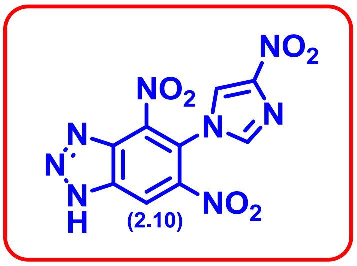
^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.304 (s, 1H).

^{13}C NMR (100MHz, DMSO)	: δ δ (ppm) 146.03, 143.04, 129.72, 127.93, 125.53, 121.22.
Mass	: 223.
Anal. Calcd. for $C_6H_2N_6O_4$	: C, 32.44; H, 0.91; N, 37084.
Found	: C, 32.56; H, 1.06; N, 37.71.

General procedure for the catalytic N-arylation of substituted azoles with 4,6-dinitro-5-chloro-1H-benzo[1,2,3]triazole (2.3)

A round bottom flask with a magnetic stirrer charged with CuI (8.0 mg, 0.2 mmol), Cs_2CO_3 (0.422 g, 2.0 mmol), substituted azoles (1.4 mmol), 5-chloro-1*H*-benzo [1,2,3] triazole (1.0 mmol) and DMF (1 mL) under nitrogen atmosphere. The reaction mixture was stirred at 110-120 ˚C for 24h and then diluted with 3 ml of ethyl acetate, filtered through a plug of silica gel and washed with 10-20 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

***4,6-Dinitro-5-(4-nitro-1H-imidazol-1-yl)-1H-benzo[d][1,2,3]triazole* (2.10):** 4-Nitroim- idazole (0.325 g, 2.8 mmol), 5-chloro-1*H*-benzo[1,2,3]triazole (0.500 g, 2.0 mmol) CuI (0.078 mg, 0.41 mmol), Cs_2CO_3 (1.34 g, 4.1 mmol) and DMF (2 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure colour compound (**2.10**). (0.320g, 48.6% yield). Melting point: 132 ˚C.



IR (KBr pellet, ν_{max}/cm^{-1})	: 3483, 3142, 3015, 2881, 2820, 1730, 1631, 1556, 1493, 1433, 1381, 1334, 1253, 1224, 1086, 989, 945, 866, 817, 787, 758, 698.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.143 (s, 1H), 8.214(s, 1H), 7.765 (s, 1H).

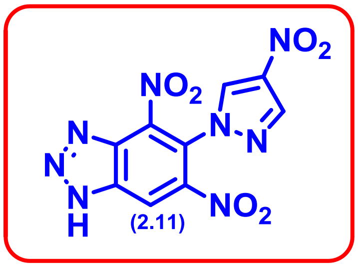
^{13}C NMR (100MHz, DMSO) : δ (ppm) 147.69, 146.16, 136.25, 134.29, 132.25, 131.99, 121.76, 119.66, 119.37.

Mass : 321.

Anal. Calcd. for $C_9H_4N_8O_6$: C, 33.76; H, 1.26; N, 35.00

Found : C, 33.65; H, 1.21; N, 35.11.

4,6-Dinitro-5-(3-nitro-1H-pyrazole -1-yl)-1H-benzo[d][1,2,3]triazole (2.11): 4-Nitro- pyrazole (0.142 g, 1.2 mmol), 5-chloro-1*H*-benzo[1,2,3]triazole (0.235 g, 1.96 mmol) CuI (0.0368 g, 1.9 mmol), Cs_2CO_3 (0.630 g, 1.93 mmol) and DMF (1.5 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure compound (**2.11**). (0.180 g, 58% yield). Melting point: 168 ˚C.



(2.11)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3130, 2934, 2405, 1984, 1880, 1643, 1548, 1518, 1404, 1385, 1342, 1282, 1215, 1109, 1060, 112, 949, 873, 815, 787, 748, 704, 669, 590.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.326 (s, 1H), 9.185(s, 1H), 8.465 (s, 1H).

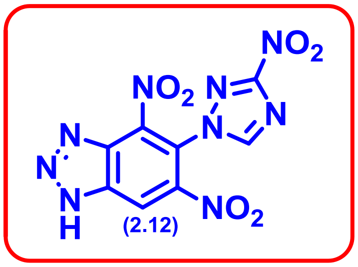
^{13}C NMR (100MHz, DMSO) : δ (ppm) 143.82, 142.78, 137.76, 137.54, 133.79, 131.36, 130.58, 125.19, 121.46.

Mass : 321.

Anal. Calcd. for $C_9H_4N_8O_6$: C, 33.76; H, 1.26; N, 35.00.

Found : C, 37.61; H, 1.32; N, 35.12.

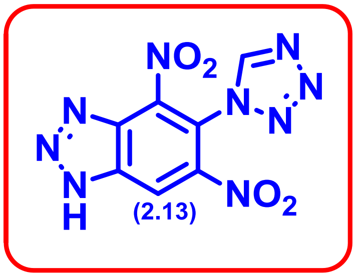
4,6-dinitro-5-(3-nitro-1H-1,2,4-triazol-1-yl)-1H-benzo[d][1,2,3]triazole (2.12): 3-Nitro -1,2,4-triazole (0.112 g, 0.98 mmol), 5-chloro-1*H*-benzo[1,2,3]triazole (0.200 g, 0.82 mmol) CuI (0.031 g, 0.16 mmol), Cs_2CO_3 (0.536 g, 1.6 mmol) and DMF (1.5 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure compound (**2.12**). (0.180 g, 68% yield). Melting point: 160 ˚C.



(2.12)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3402, 2958, 2909, 2849, 1742, 1709, 1610, 1545, 1463, 1342, 1260, 1090, 1019, 882, 794.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 9.331 (s, 1H), 8.894 (s, 1H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 156.03, 150.87, 146.68, 144.58, 133.15, 131.69, 122.11, 121.12.
Mass	: 322.
Anal. Calcd. for $C_8H_3N_9O_6$	: C, 29.92; H, 0.94; N, 39.25; O, 29.89.
Found	: C, 29.85; H, 1.06; N, 39.15.

***4,6-Dinitro-5-(1H-tetrazol-1-yl)-1H-benzo[d][1,2,3]triazole* (2.13):** 1*H*-Tetrazole (0.0376 g, 0.53 mmol), 5-chloro-1*H*-benzo[1,2,3]triazole (0.100 g, 0.41 mmol) CuI (0.0156 g, 0.081 mmol), Cs_2CO_3 (0.267 g, 0.82 mmol) and DMF (1 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure compound (**2.13**). (0.060 g, 53% yield). Melting point: 140 ˚C.

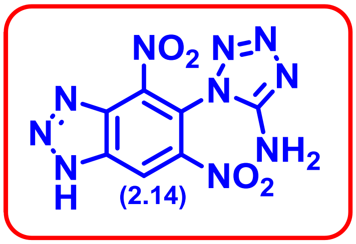


(2.13)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3402, 2958, 2920, 2849, 1742, 1704, 1550, 1457, 1347, 1260, 1095, 1030, 876, 805, 734, 701.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 9.301 (s, 1H), 8.530 (s, 1H).

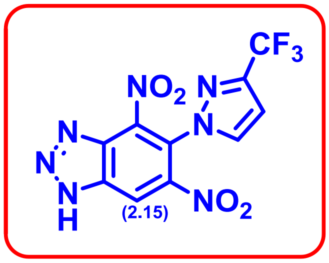
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 146.36, 138.31, 134.87, 132.28, 121.58, 120.77, 114.03.
Mass	: 278.
Anal. Calcd. for $C_7H_3N_9O_4$	: C, 30.33; H, 1.09; N, 45.48.
Found	: C, 30.18; H, 1.16; N, 45.56.

***1-(4,6-Dinitro-1H-benzo[d][1,2,3]triazol-5-yl)-1H-tetrazol-5-amine* (2.14):** 2-Amino-1*H*-tetrazole (0.041 g, 0.49 mmol), 5-chloro-1*H*-benzo[1,2,3]triazole (0.100 g, 0.41 mmol) CuI (0.0156 g, 0.082 mmol), Cs_2CO_3 (0.267 g, 0.82 mmol) and DMF (1 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure compound (**2.14**). (0.060 g, 50% yield). Melting point: 160 ˚C.



IR (KBr pellet, ν_{max}/cm^{-1})	: 3342, 3080, 2924, 2854, 2258, 1741, 1633, 1548, 1464, 1342, 1263, 1224, 1024, 821, 702.
^1H NMR (400 MHz, DMSO)	: δ (ppm) 9.356 (s, 2H), 9.146 (s, 1H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 162.75, 146.30, 138.32, 134.85, 128.24, 119.77, 114.02.
Mass	: 293.
Anal. Calcd. for $C_7H_4N_{10}O_4$	: C, 28.78; H, 1.38; N, 47.94.
Found	: C, 28.61; H, 1.41; N, 47.85.

***4,6-Dinitro-5-(trifluoromethyl)-1H-pyrazol-1-yl)-1-H benzo[d][1,2,3]triazole* (2.15):** 3-Trifluoromethyl-1*H*-pyrazole (0.100 g, 0.74 mmol), 5-chloro-1*H*-benzo[1,2,3]triazole (0.150 g, 0.61 mmol) CuI (0.0235 g, 0.123 mmol), Cs_2CO_3 (0.401 g, 1.23 mmol) and DMF (1 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure compound (**2.15**). (0.110 g, 53% yield). Melting point 182 ˚C.



(2.15)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3339, 3121, 2926, 2854, 2256, 2129, 1739, 1633, 1550, 1477, 1390, 1342, 1304, 1265, 1143, 1026, 968, 821, 777, 742.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.171 (s, 1H), 8.561 (d, *J* 2, 1H), 7.132 (d, *J* 3, 1H).

^{19}F NMR (400 MHz, DMSO) : δ (ppm) -60.850.

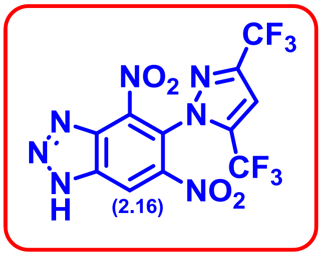
^{13}C NMR (100MHz, DMSO) : δ (ppm) 162.86, 144.60, 144.30, 142.98, 137.35, 137.27, 131.90, 122.48, 120.35,107.12.

Mass : 344.

Anal. Calcd. for $C_{10}H_4F_3N_7O_4$: C, 35; H, 1.17; N, 28.57.

Found : C, 35.11; H, 1.23; N, 28.5.

5-(2,4-bis(trifluoromethyl)-1H-imidazol-1-yl)-4,6-dinitro-1H-benzo[d][1,2,3] triazole (2.16):
3,5-Bis(trifluoromethyl)-1*H*-pyrazole(0.117 g, 0.57 mmol),5-chloro-1*H*-benzo[1,2,3]tr-iazole (0.100 g, 0.41 mmol) CuI (0.0156 g, 0.082 mmol), Cs_2CO_3 (0.267 g, 0.82 mmol) and DMF (1 mL) were subjected to the general method to give crude product. The crude product was purified over a silica gel column with ethyl acetate/hexane to obtain pure compound (**2.16**). (0.090 g, 54% yield). Melting point: 178 ˚C.


(2.16)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3412, 2926, 2856, 2590, 2254, 2127, 1711, 1658, 1548, 1348, 1313, 1275, 1026, 825, 763.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.167 (s, 1H), 7.956 (s, 1H).

^{19}F NMR (400 MHz, DMSO) : δ (ppm) -61.40, -59.60.

^{13}C NMR (100MHz, DMSO) : δ (ppm) 170.07, 164.90, 162.77, 138.28, 134.88, 128.27,124.77, 124.67, 118.90, 114.00.

Mass : 412.

Anal. Calcd. for $C_{11}H_3F_6N_7O_4$: C, 32.13; H, 0.74; N, 23.85.

Found : C, 32.21; H, 0.82; N, 23.76.

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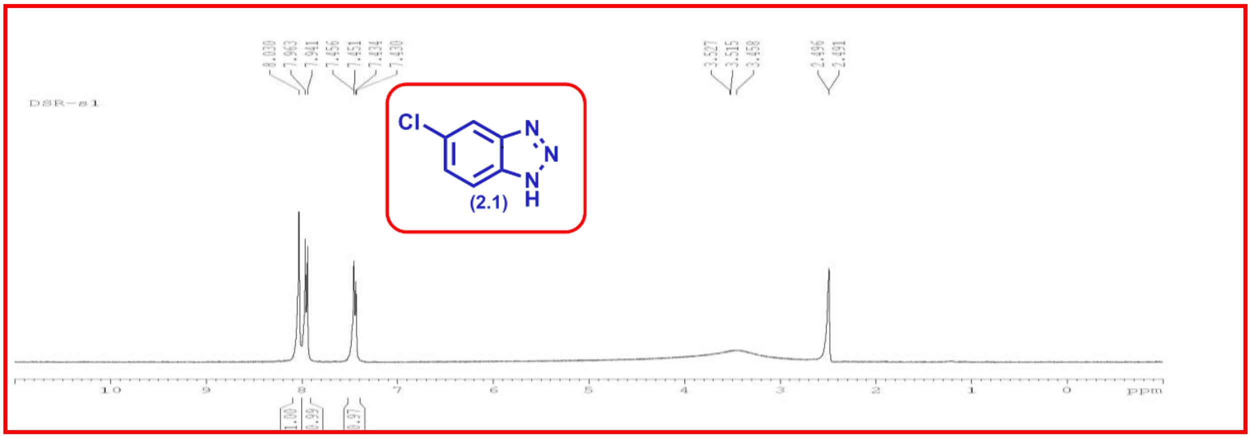


Figure 2.S1 *^{1}H NMR spectrum of 5-chloro-1H-benzo[1,2,3]triazole (**2.1**)*

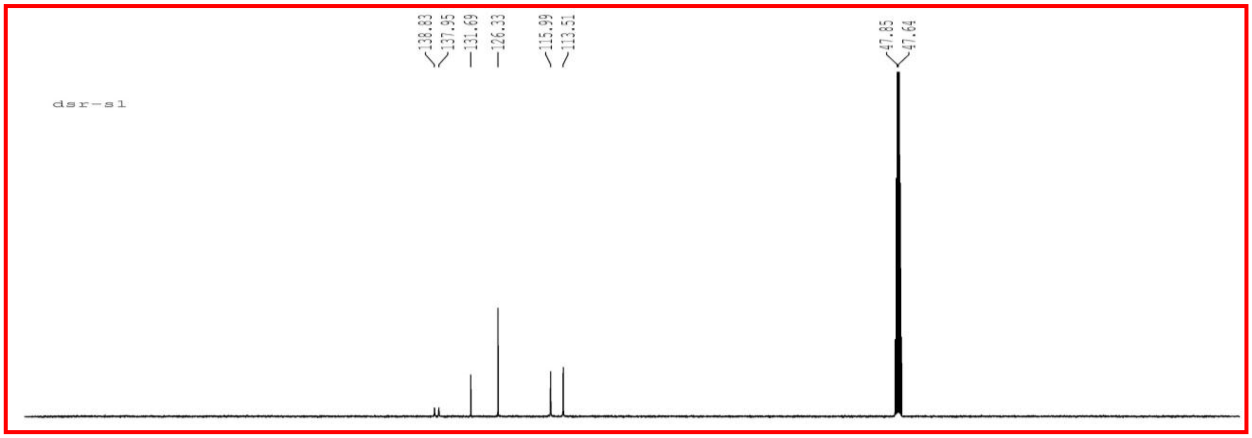


Figure 2.S2 *^{13}C NMR spectrum of 5-chloro-1H-benzo[1,2,3]triazole (**2.1**)*

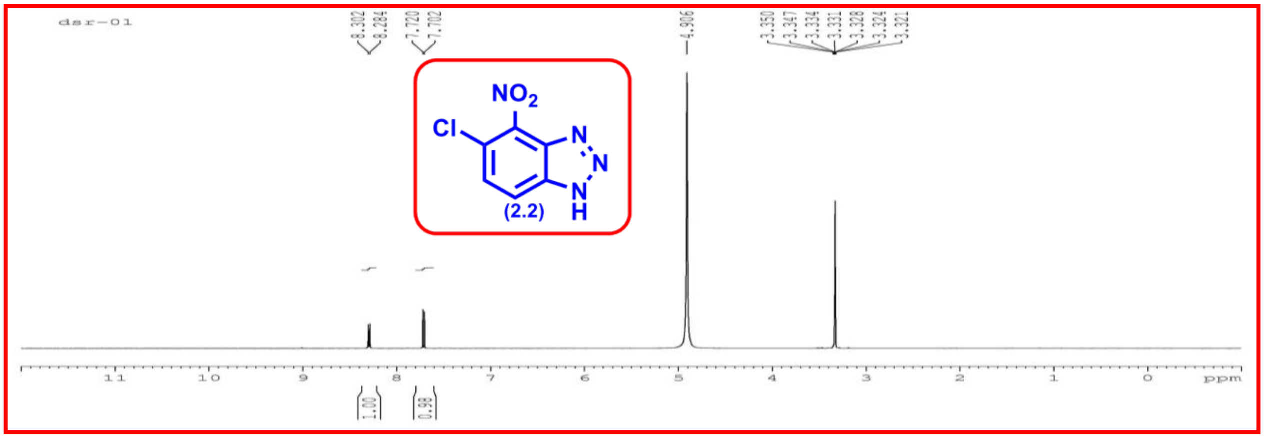


Figure 2.S3 *^{1}H NMR spectrum of 5-Chloro-4-nitro-1H-benzo[1,2,3]triazole (**2.2**)*

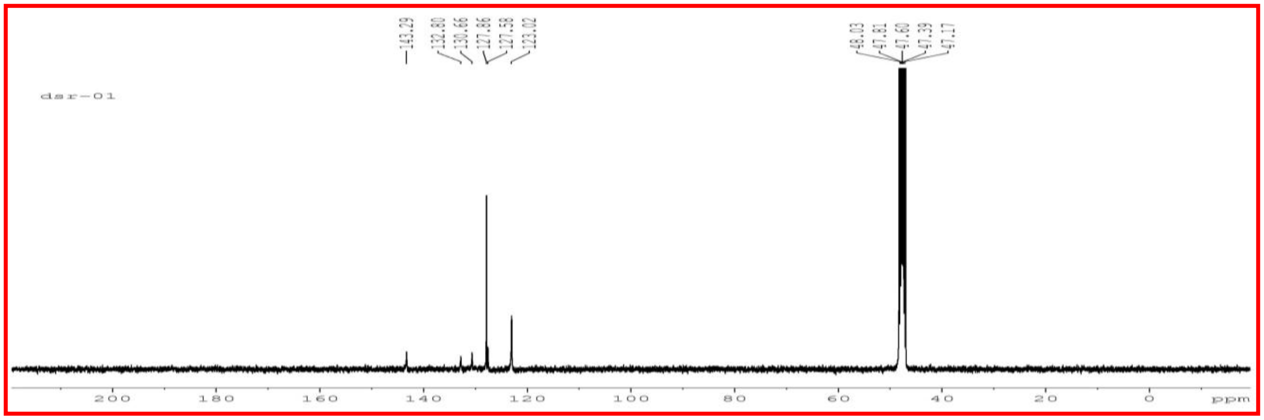


Figure 2.S4 *^{13}C NMR spectrum of 5-Chloro-4-nitro-1H-benzo[1,2,3]triazole (**2.2**)*

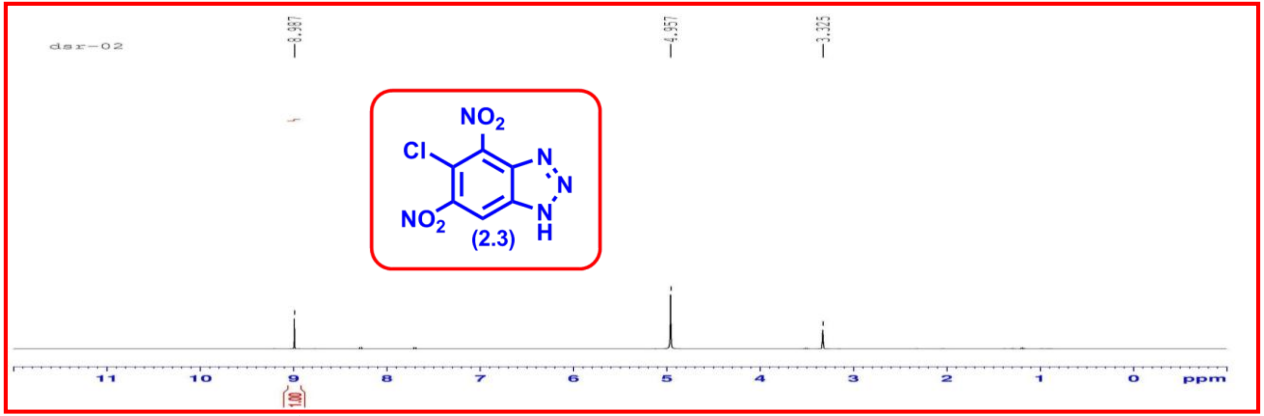


Figure 2.S5 *^{1}H NMR spectrum of 5-Chloro-4, 6-dinitro-1H-benzo[1,2,3]triazole (**2.3**)*

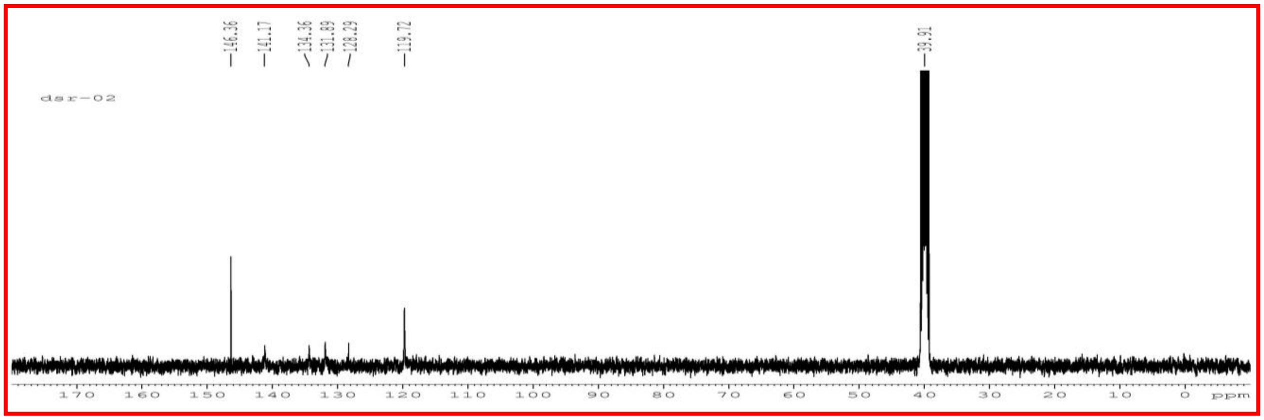


Figure 2.S6 *^{13}C NMR spectrum of 5-Chloro-4, 6-dinitro-1H-benzo[1,2,3]triazole (**2.3**)*

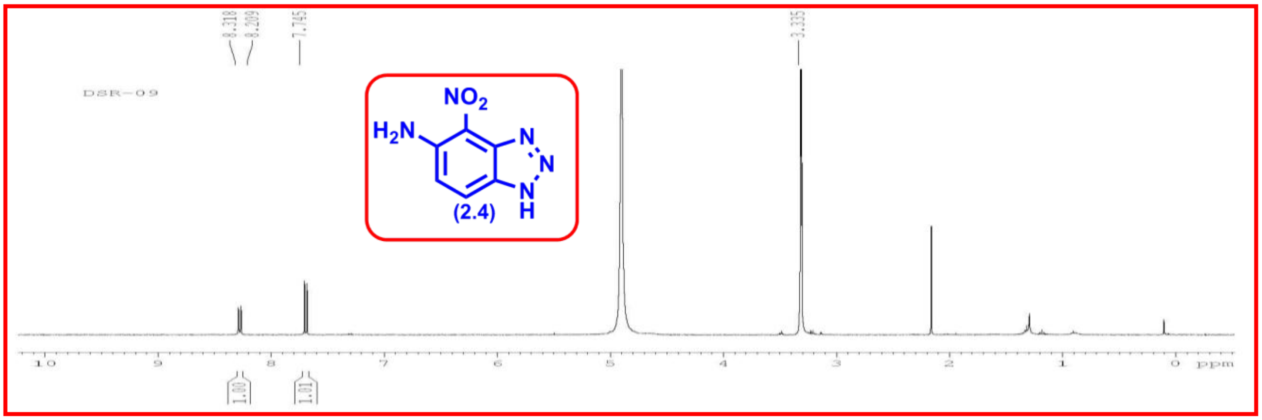


Figure 2.S7 *^{1}H NMR spectrum of 4-Nitro-1H-benzo[1,2,3]-5-amine (**2.4**)*

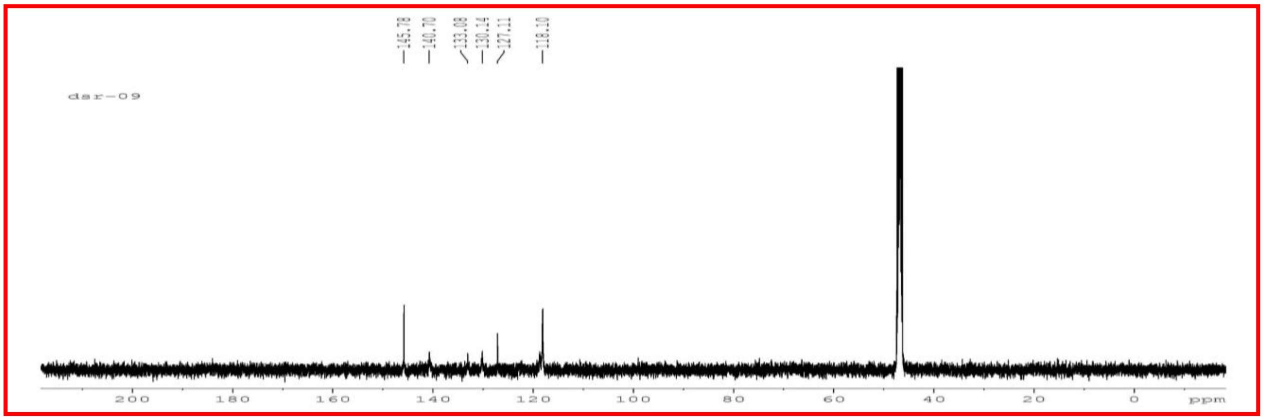


Figure 2.S8 *^{13}C NMR spectrum of 4-Nitro-1H-benzo[1,2,3]-5-amine (**2.4**)*

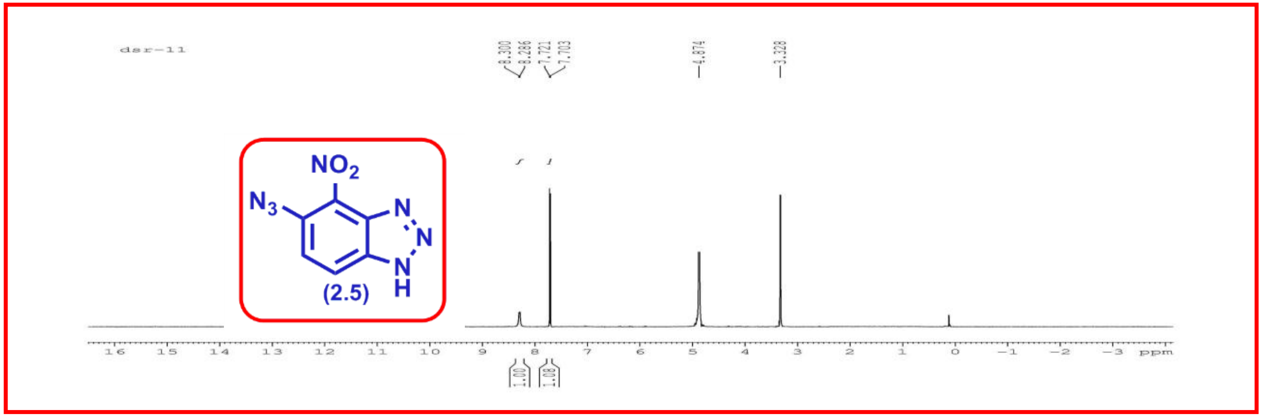


Figure 2.S9 *^{1}H NMR spectrum of 5-Azido-4-nitro-1H-benzo[1,2,3]triazole (**2.5**)*

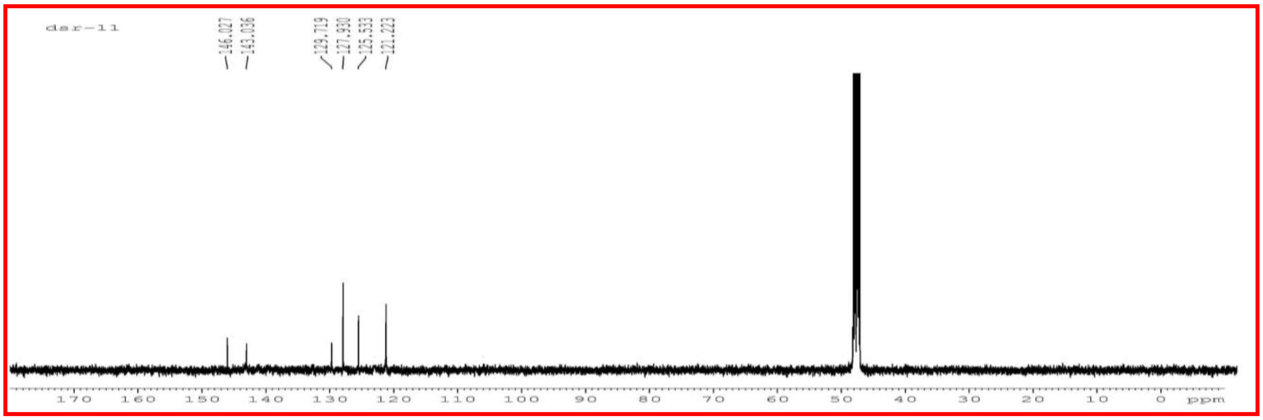


Figure 2.S10 *^{13}C NMR spectrum of 5-Azido-4-nitro-1H-benzo[1,2,3]triazole (**2.5**)*

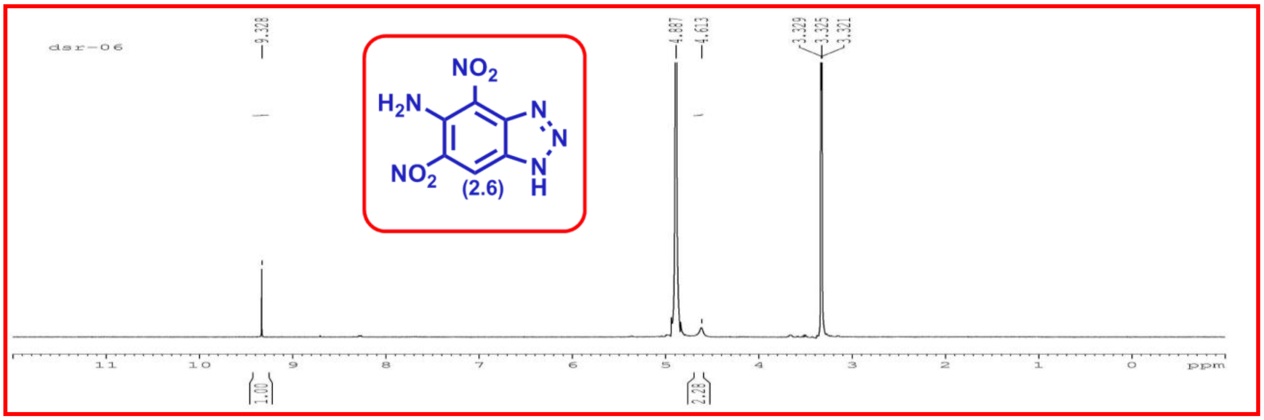


Figure 2.S11 *^{1}H NMR spectrum of 4,6-Dinitro-1H-benzo[1,2,3]-5-amine (**2.6**)*

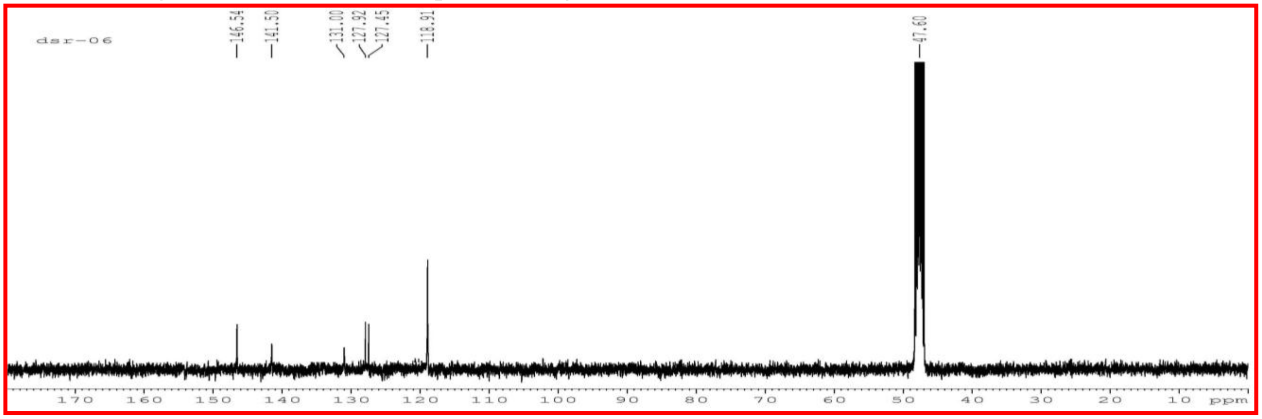


Figure 2.S12 *^{13}C NMR spectrum of 4,6-Dinitro-1H-benzo[1,2,3]-5-amine (**2.6**)*

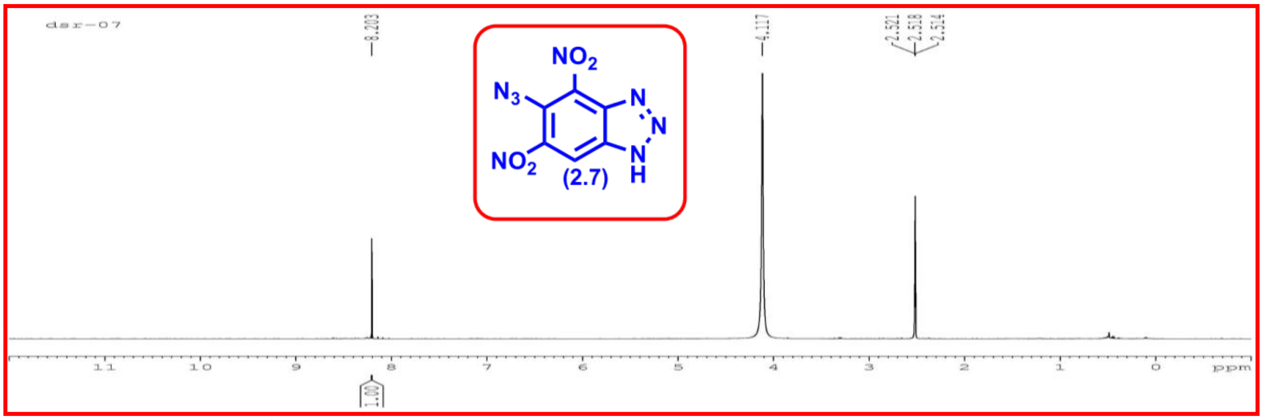


Figure 2.S13 *^{1}H NMR spectrum of 5-Azido-4,6-dinitro-1H-benzo[1,2,3]triazole (**2.7**)*

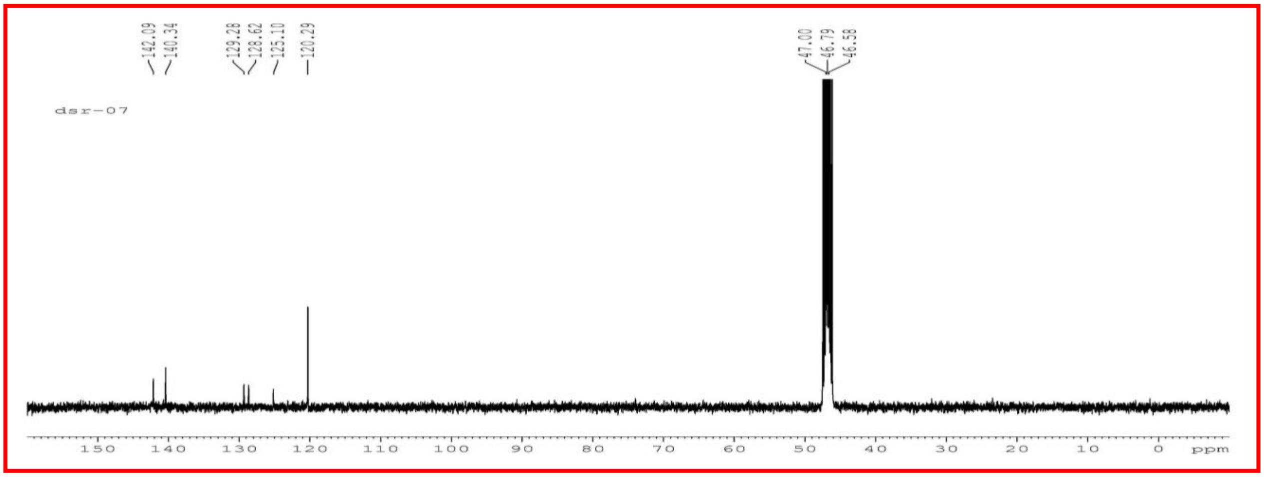


Figure 2.S14 *^{13}C NMR spectrum of 5-Azido-4,6-dinitro-1H-benzo[1,2,3]triazole (**2.7**)*

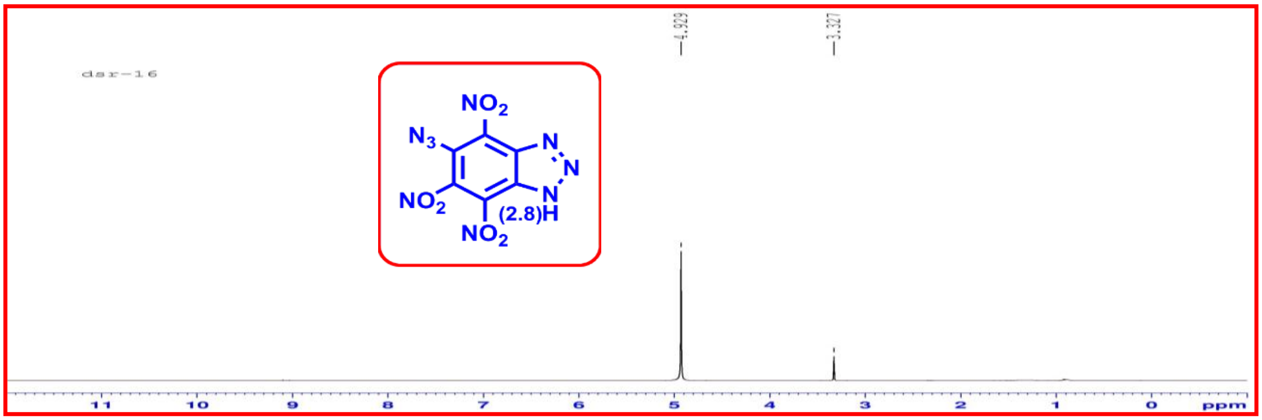


Figure 2.S15 *^{1}H NMR spectrum of 5-Azido-4,6,7-trinitro-1H-benzo[1,2,3]triazole (**2.8**)*

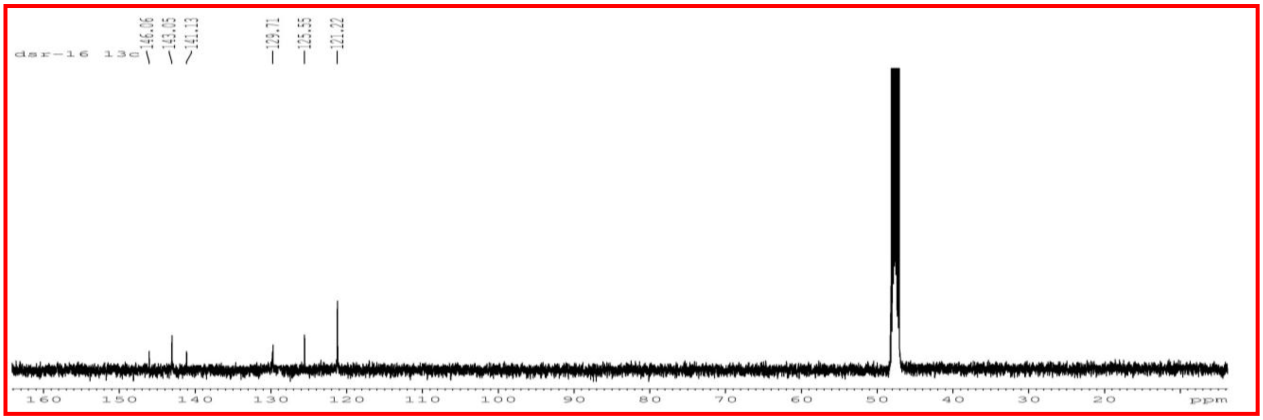


Figure 2.S16 *^{13}C NMR spectrum of 5-Azido-4,6,7-trinitro -1H-benzo[1,2,3]triazole (**2.8**)*

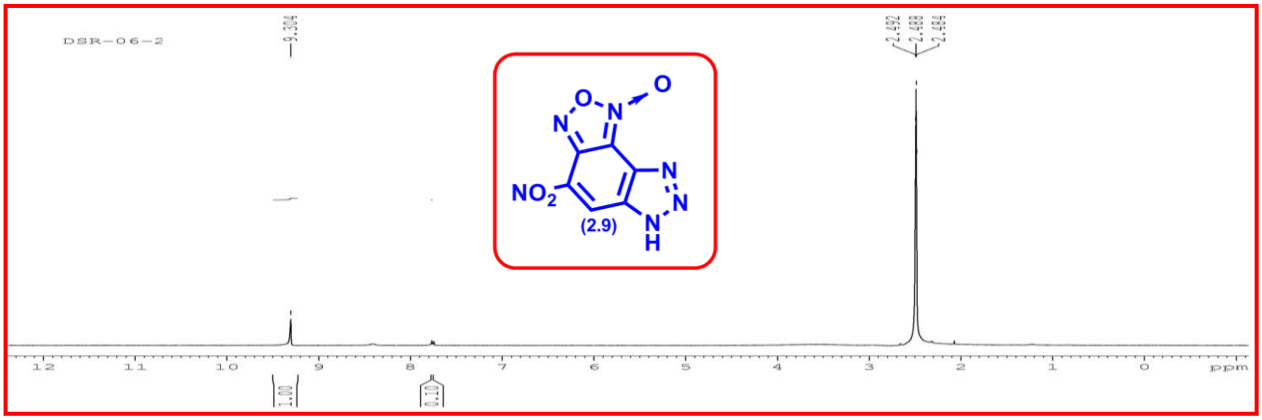


Figure 2.S17 *^{1}H NMR spectrum of 4-Nitro-6H-[1,2,3]triazolo[4,5-e][2,1,3]benzoxadiazole 1-oxide (**2.9**)*

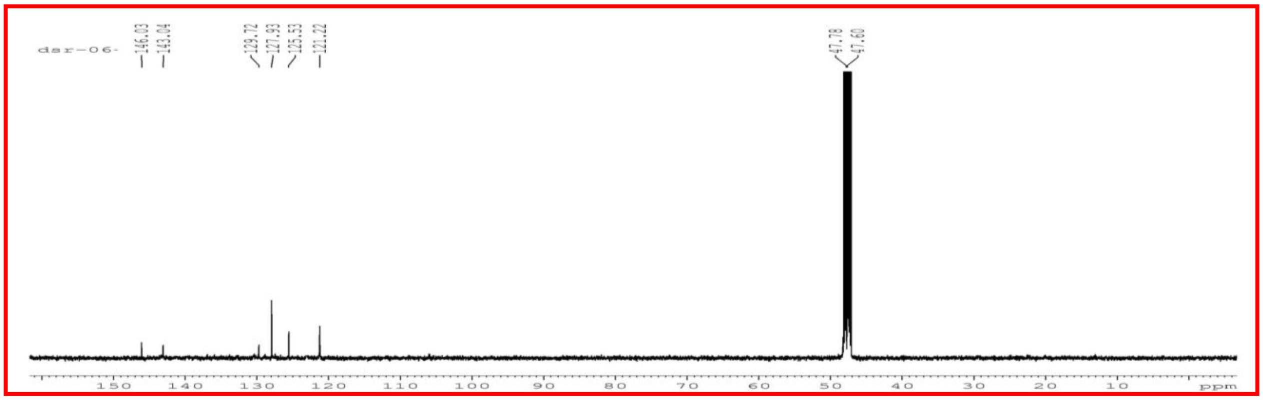


Figure 2.S18 *^{13}C NMR spectrum of 4-Nitro-6H-[1,2,3]triazolo[4,5-e][2,1,3]benzoxadiazole 1-oxide (**2.9**)*

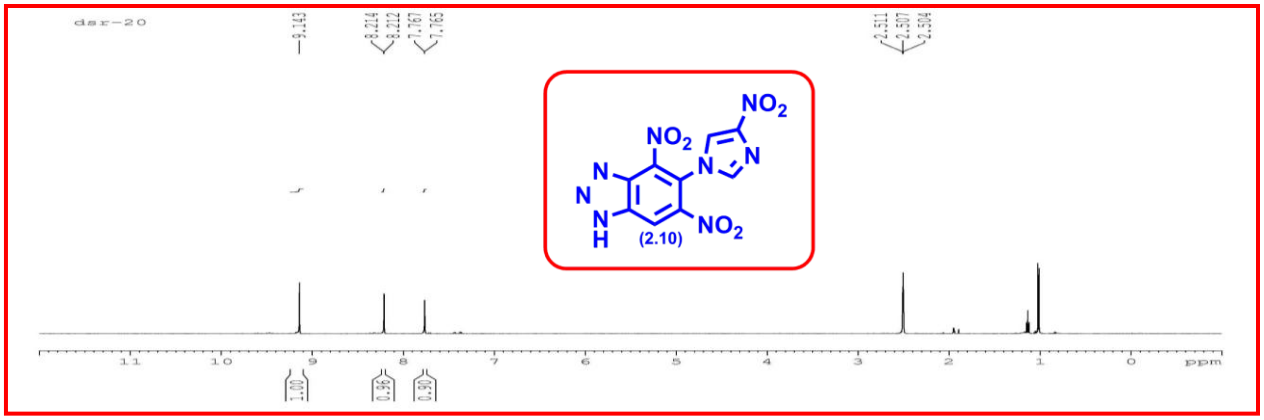


Figure 2.S19 *^{1}H NMR spectrum of 4,6-dinitro-5-(4-nitro-1H-imidazol-1-yl)-1H-benzo[d] [1,2,3] triazole (**2.10**)*

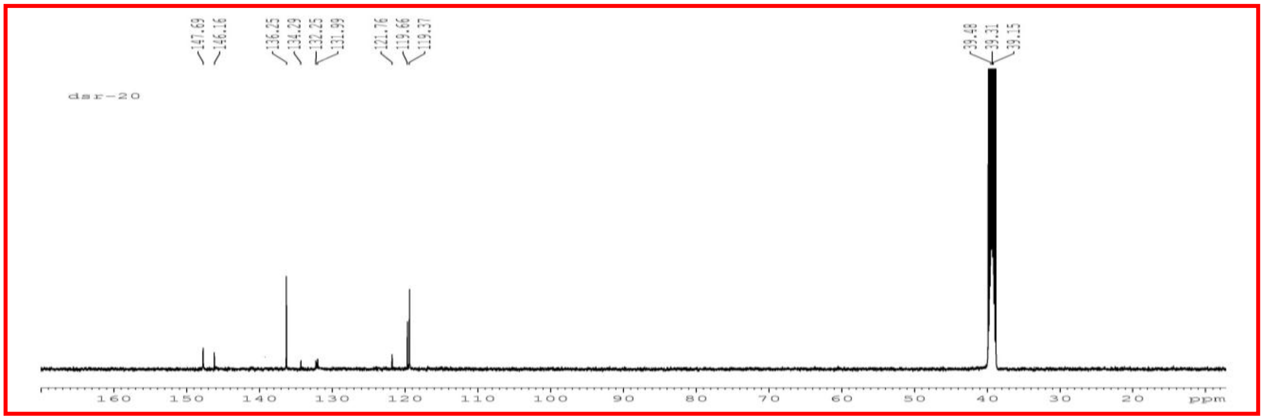


Figure 2.S20 *^{13}C NMR spectrum of 4,6-dinitro-5-(4-nitro-1H-imidazol-1-yl)-1H-benzo[d] [1,2,3] triazole (**2.10**)*

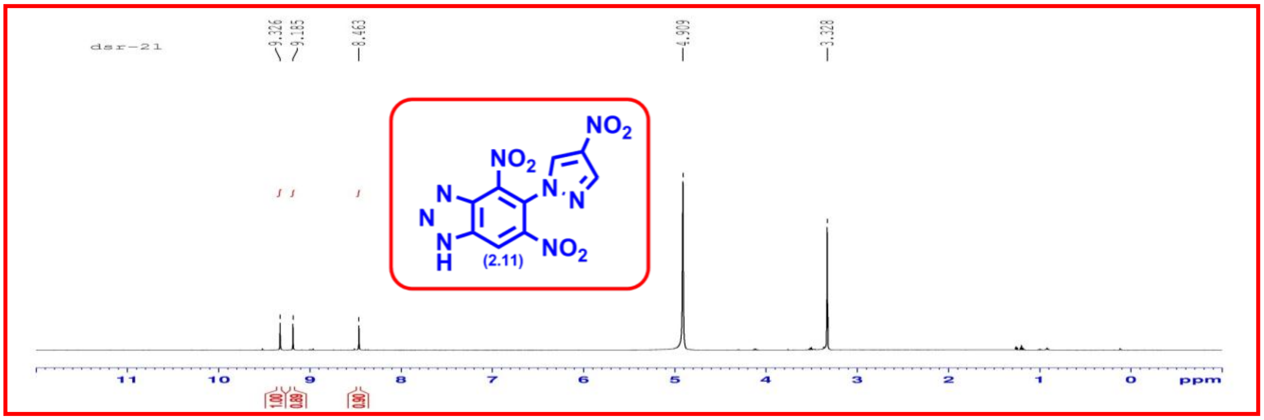


Figure 2.S21 *^{1}H NMR spectrum of 4,6-dinitro-5-(3-nitro-1H-pyrazole -1-yl)-1H-benzo[d] [1,2,3] triazole (**2.11**)*

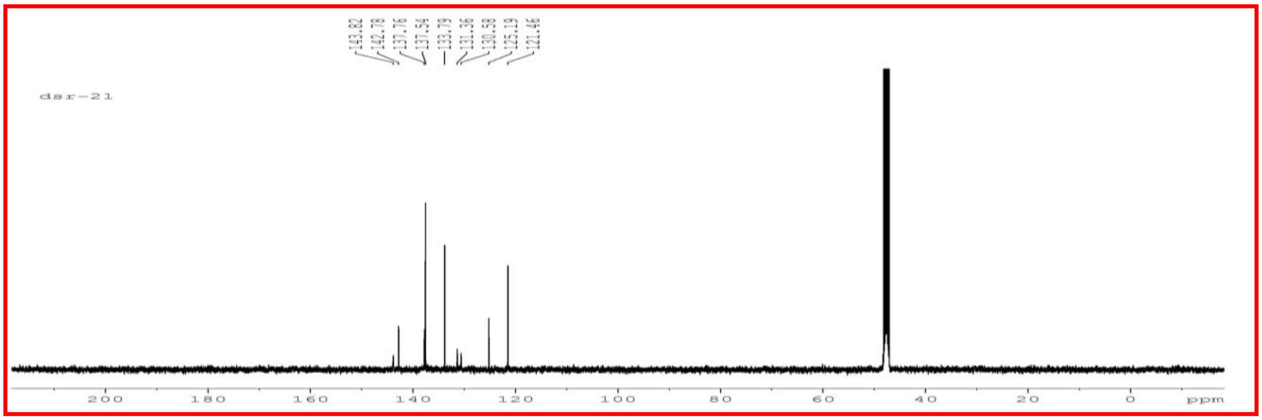


Figure 2.S21 *^{13}C NMR spectrum of 4,6-dinitro-5-(3-nitro-1H-pyrazole -1-yl)-1H-benzo[d] [1,2,3] triazole (**2.11**)*

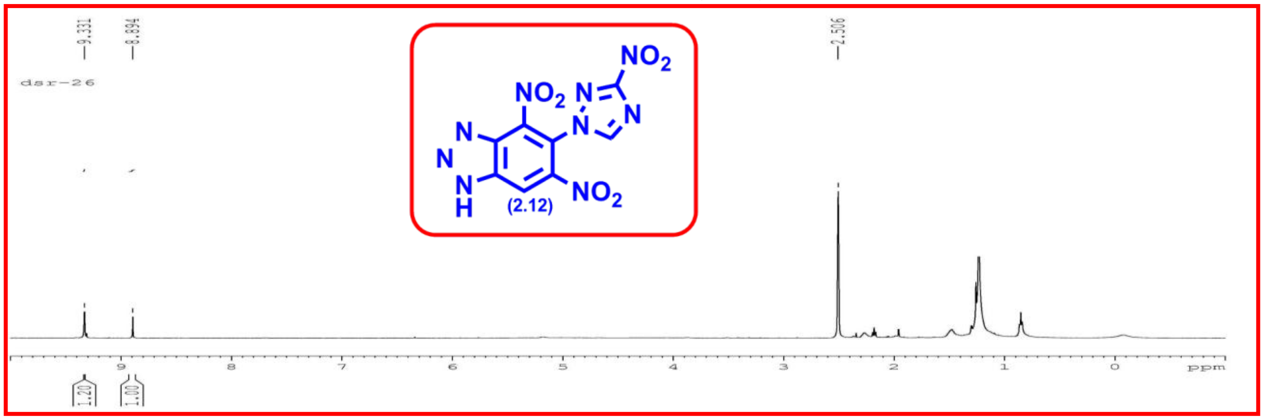


Figure 2.S23 *^{1}H NMR spectrum of 4,6-dinitro-5-(3-nitro-1H-1,2,4-triazol-1-yl)-1H-benzo[d][1,2,3]triazole (**2.12**)*

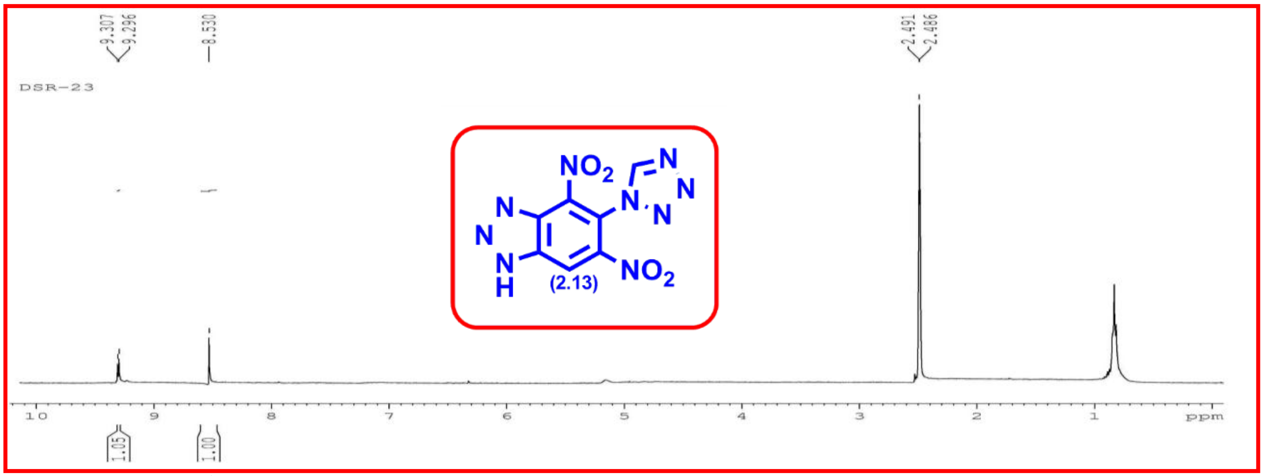


Figure 2.S25 *^{1}H NMR spectrum of 4,6-dinitro-5-(1H-tetrazol-1-yl)-1H-benzo[d][1,2,3]triazole (**2.13**)*

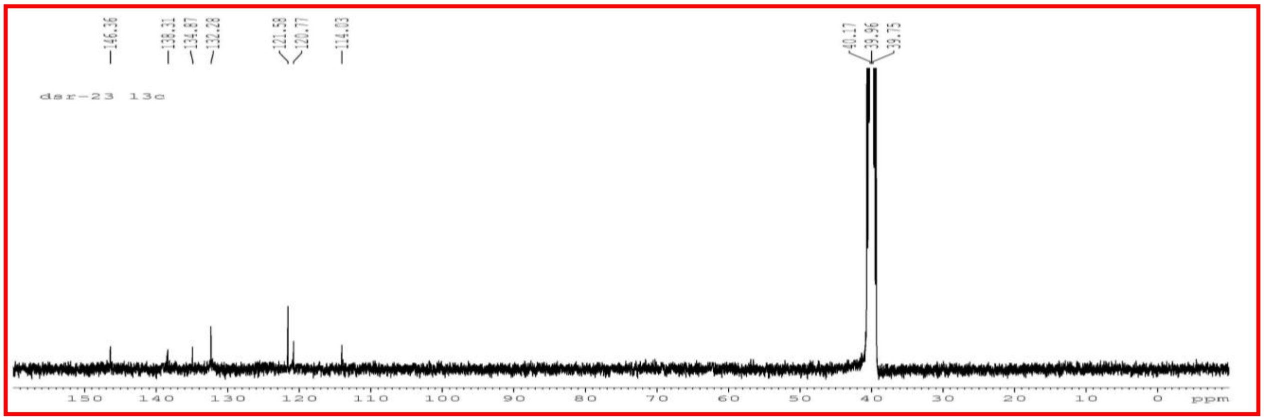


Figure 2.S25 *^{13}c NMR spectrum of 4,6-dinitro-5-(1H-tetrazol-1-yl)-1H-benzo[d][1,2,3]triazole (**2.13**)*

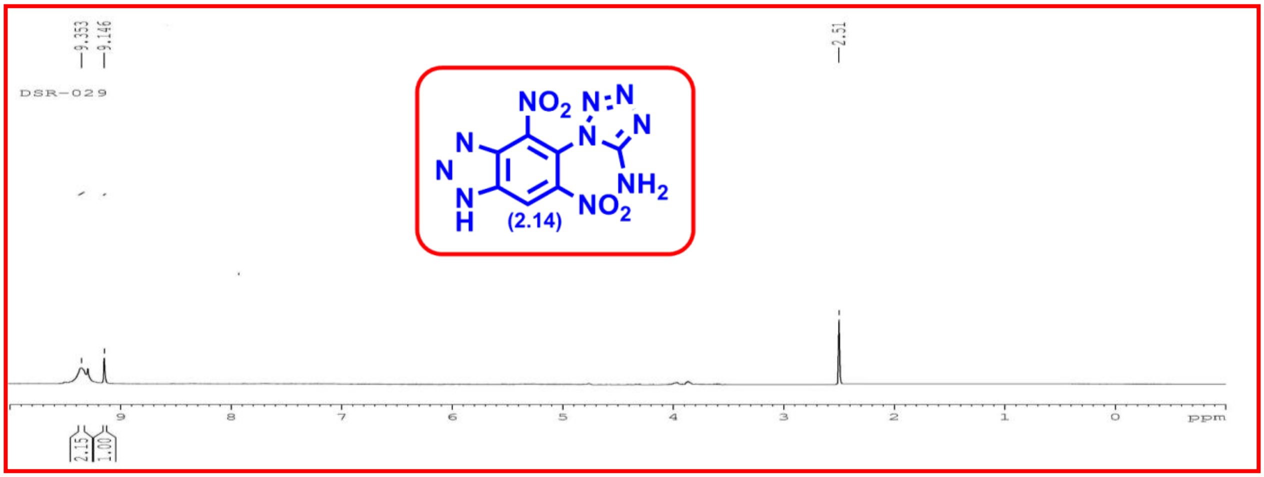


Figure 2.S27 *^{1}H NMR spectrum of 1-(4,6-dinitro-1H-benzo[d][1,2,3]triazol-5-yl)-1H-tetrazol-5-amine (**2.14**)*

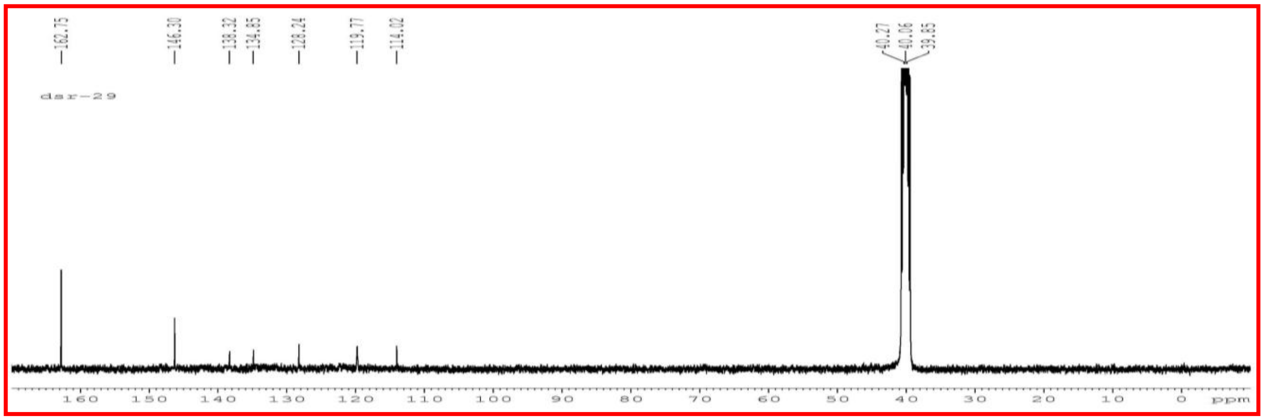


Figure 2.S28 *^{13}C NMR spectrum of 1-(4,6-dinitro-1H-benzo[d][1,2,3]triazol-5-yl)-1H-tetrazol-5-amine (**2.14**)*

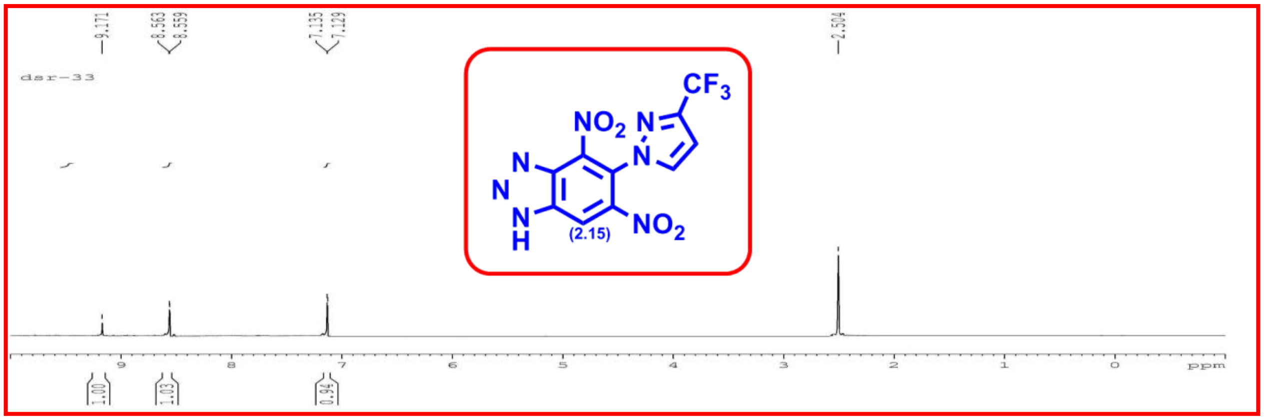


Figure 2.S29 ^{1}*H NMR spectrum of 4,6-dinitro-3-(trifluoromethyl)-1H-pyrazol-1-yl)-1-H benzo[d][1,2,3]triazole (**2.15**)*

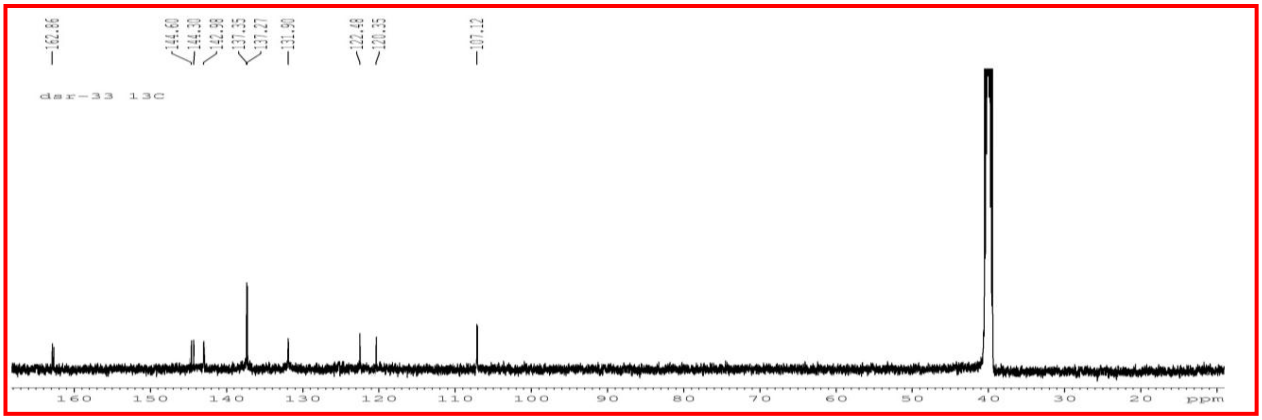


Figure 2.S30 ^{13}*C NMR spectrum of 4,6-dinitro-3-(trifluoromethyl)-1H-pyrazol-1-yl)-1-H benzo[d][1,2,3]triazole (**2.15**)*

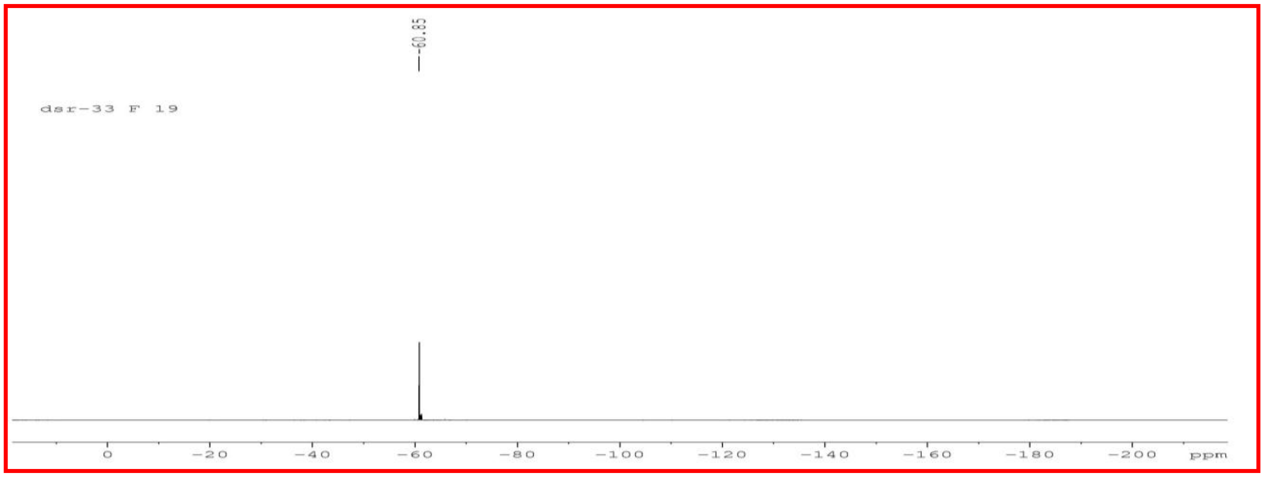


Figure 2.S31 ^{19}*F NMR spectrum of 4,6-dinitro-3-(trifluoromethyl)-1H-pyrazol-1-yl)-1-H benzo[d][1,2,3]triazole (**2.15**)*

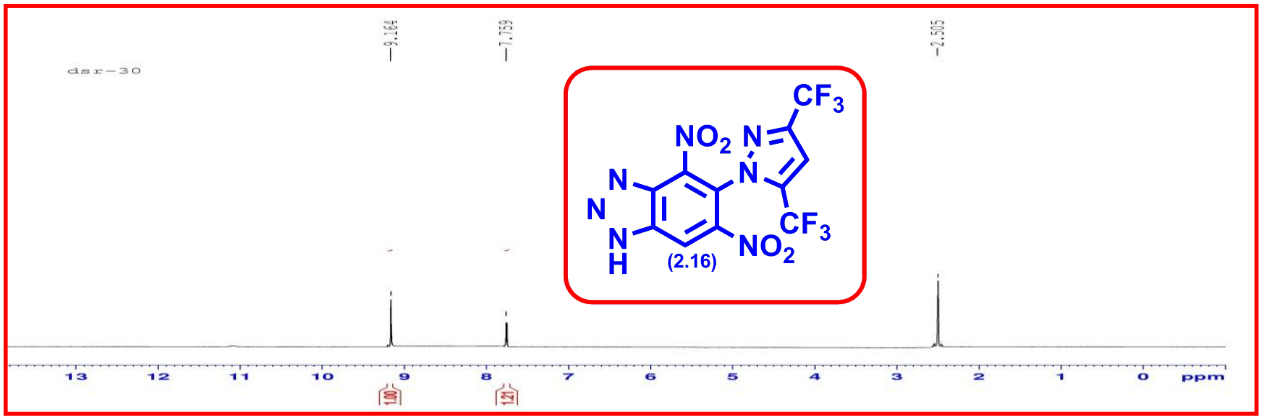


Figure 2.S32 *^{1}H NMR spectrum of 5-(2,4-bis(trifluoromethyl)-1H-imidazol-1-yl)-4,6-dinitro-1H-benzo[d][1,2,3]triazole (**2.16**)*

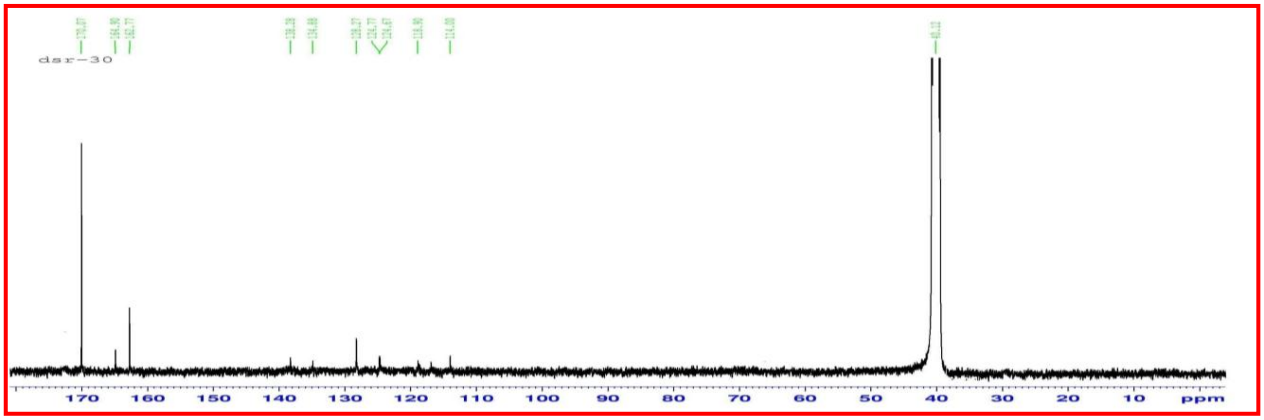


Figure 2.S33 *^{13}C NMR spectrum of 5-(2,4-bis(trifluoromethyl)-1H-imidazol-1-yl)-4,6-dinitro-1H-benzo[d][1,2,3]triazole (**2.16**)*

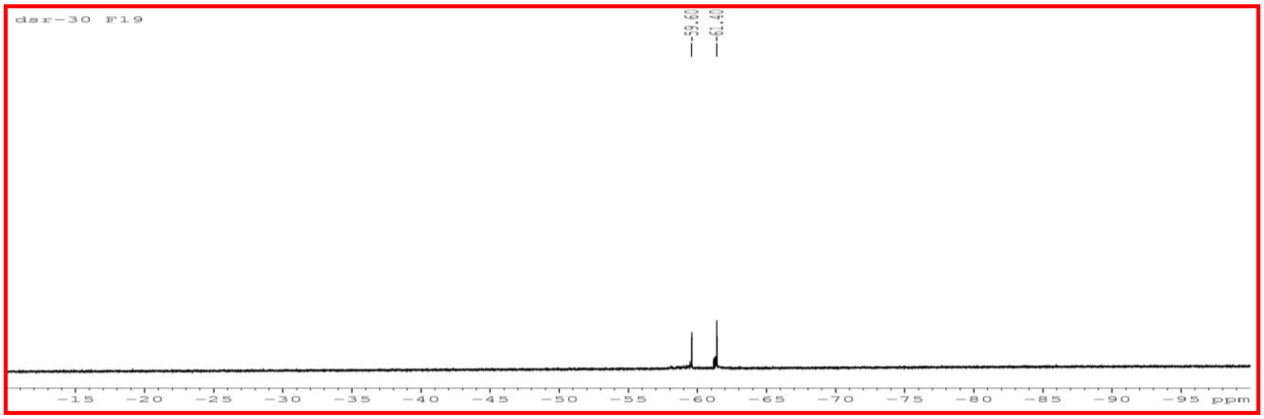


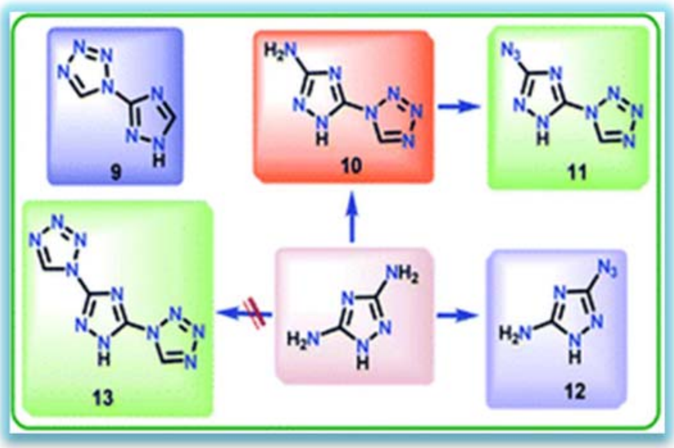
Figure 2.S34 *^{19}F NMR spectrum of 4,6-dinitro-3-(trifluoromethyl)-1H-pyrazol-1-yl)-1-H benzo[d][1,2,3]triazole (**2.16**)*

CHAPTER 3

Synthesis of nitrogen-rich imidazole, 1, 2, 4-triazole and tetrazole-based compounds

Abstract

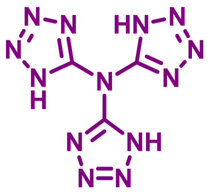
Imidazole, 1,2,4-triazole and tetrazole based molecules were prepared for their possible applications in nitrogen-rich energetic materials and gas generators. The energetic salts of 1-(1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole (**3.9**), 5-(1*H*-tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine (**3.10**), 1-(3-azido-1*H*-1,2,4-triazol-5-yl)-1*H*-tetrazole (**3.11**) and 3-azido-1*H*-1,2,4-triazol-5-amine (**3.12**) were prepared with various cationic moieties. Their densities, heats of formation, chemical energy of detonation, detonation velocities and pressures were calculated. All of the compounds possess high positive heats of formation due to high energy contribution from the molecular backbone of the corresponding compounds. The effect of the azole rings and nitro, amino, and azido groups on their physicochemical properties was examined and discussed.



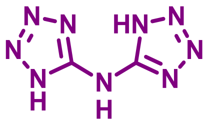
3.1. Introduction

In recent years, the development of heterocyclic based energetic compounds has attracted much attention, since these compounds offer a high positive heat of formation, density and better oxygen balance than their hydrocarbon analogs [1]. Apart from high heats of formation, nitrogen-rich compounds mainly generate environmentally friendly molecular nitrogen as a major end-product of combustion or explosion. Performance and safety during handling and usage are the most important concern in the development of energetic materials, but there is an essential contradiction between them. For example, the well-known cage and strained energetic material, CL-20 exhibit very high density (r ¼ 2.04 gcm^{-3}) and detonation performance (D ¼ 9.5 kms^{-1} and P ¼ 45 GPa), however tend to be sensitive towards impact or friction or external stimuli, whereas the less energetic materials like TNT or TATB show the opposite trend. The power of energetic materials is strongly dependent on its molecular structure and chemical substituents on it. But their safety mechanism is much more complicated and controlled by many factors. Five-membered nitrogen-containing heterocycles such as imidazole, pyrazole, triazole and tetrazole are known as traditional source of energetic materials. They are at the forefront of high energy materials research and expected to achieve increasing performance requirements with reasonable safety [2].

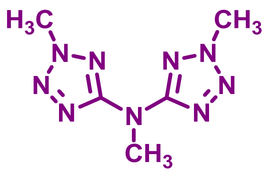
Among these heterocyclic compounds, tetrazole is a powerful building block for high energy density materials (HEDMs) due to its high nitrogen content (80%), high positive heat of formation (320 kJmol^{-1}), low sensitivity towards impact and good thermal stability due to its aromatic ring system [3]. This allows substitution of various energetic groups or designing of compounds with varying performance and sensitivity. Due to its significant energetic properties, a variety of tetrazole-based energetic compounds have already been synthesized. Moreover, introduction of nitro, azido or azo groups, salt formation and N-oxidation in tetrazole have been developed to improve the properties of tetrazole-based energetic materials. Due to high nitrogen content and consequently high average two electron bond energy associated with the N–N triple bond formation, these compounds have variety of applications as low-smoke producing pyrotechnic compositions [4], gas generators [5], propellants [6], and high explosives [7]. Gas



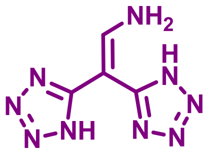
tri(1H-tetrazol-5-yl)amine



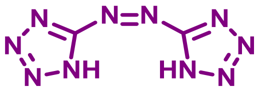
di(1H-tetrazol-5-yl)amine



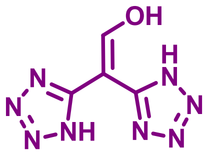
N,2-dimethyl-N-(2-methyl-2H-tetrazol-5-yl)-2H-tetrazol-5-amine



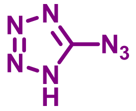
2,2-di(1H-tetrazol-5-yl)ethenamine



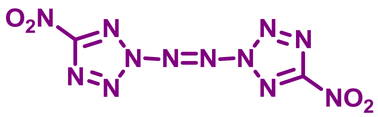
(Z)-1,2-di(1H-tetrazol-5-yl)diazene



2,2-di(1H-tetrazol-5-yl)ethanol

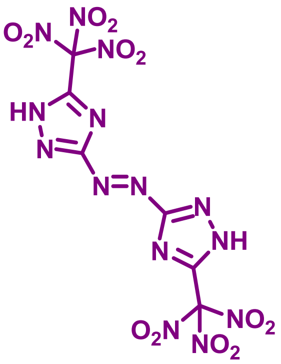


5-azido-1H-tetrazole

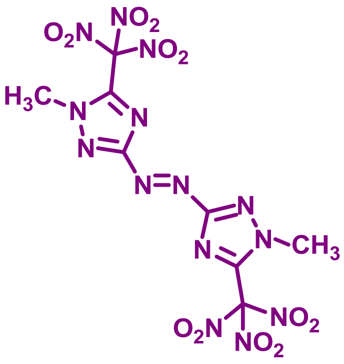


1,2-bis(5-nitro-2H-tetrazol-2-yl)diazene

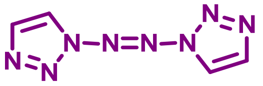
1,2-di(1H-tetrazol-1-yl)diazene



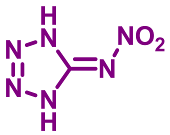
(E)-1,2-bis(5-(trinitromethyl)-1H-1,2,4-triazol-3-yl)diazene



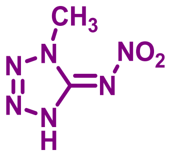
(E)-1,2-bis(1-methyl-5-(trinitromethyl)-1H-1,2,4-triazol-3-yl)diazene



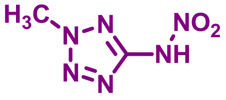
1,2-di(1H-1,2,3-triazol-1-yl)diazene



N-(1H-tetrazol-5(4H)-ylidene)nitramide



(Z)-N-(1-methyl-1H-tetrazol-5(4H)-ylidene)nitramide



N-(2-methyl-2H-tetrazol-5-yl)nitramide

Figure 3.1. *Variety of high nitrogen molecules*

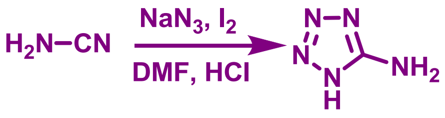
generators are used to generate large amount of gas, as for turbo pumps, to initiate balloons, especially airbags, to eject parachutes and for similar applications.

Herein, we report the synthesis of energetic salts based on the 1-(1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole (**3.9**), 5-(1*H*-tetrazol-1-yl)- 1*H*-1,2,4-triazol-3-amine (**3.10**), 1-(3-azido-1*H*-1,2,4-triazol-5-yl)- 1*H*-tetrazole (**3.11**) and 3-azido-1*H*-1,2,4-triazol-5-amine (**3.12**) anions. The presence of high nitrogen content and higher enthalpy of formation of molecules containing 1,2,3-triazoles and tetrazoles in their molecular structure would enable their use as high enthalpy modifiers in energetic materials. Further, in the recent literature, to the best of our knowledge, there is no report available exploring the synthesis of these molecules and their utility as possible nitrogen-rich energetic materials.

3.2. Results and discussion

3.2.1. Synthesis and characterization

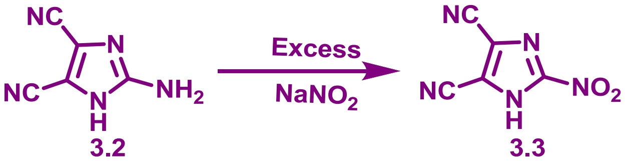
The energy content associated with the five membered azole rings makes them more essential in design and synthesis of high energy materials. The hydrogen atoms in azole rings can be substituted by amino, nitro, or azide groups to enhance their energy content and detonation performance. In this work, we are reporting the synthesis of 5-aminotetrazole (**3.1**) from cyanamide in good yield (Scheme 3.1). Previously, 5-aminotetrazole was prepared from different starting materials and its derivatives were extensively studied for their applications in energetic materials due to their high nitrogen contents and better thermal stability [8]. The cyanamide to 5-aminotetrazole conversion was carried out as described by Das et al [9]. using sodiumazide and iodine in DMF and subsequent treatment with HCl.



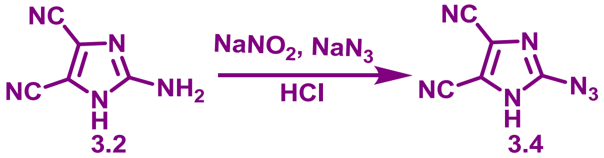
3.1

Scheme 3.1. *Formation of tetrazole from cyanamide*

High performance and low sensitivity tend to be contradicting aspects; hence it is hard to full fill all the requirements for new energetic materials. However, incorporation of azole rings into a compound is also a known strategy for increasing thermal stability and plays a very important role in designing new potential HEMs. As a result, we have synthesized different nitrogen-rich compounds, based on various imidazole–tetrazole derivatives. The 2-nitro-1*H*-imidazole-4, 5-dicarbonitrile (**3.3**) was obtained from 2-amino-1*H*- imidazole-4, 5-dicarbonitrile (**3.2**) with excess treatment of sodium nitrite [10]. Similarly **3.2** were treated with sodium nitrite followed by sodium azide to get 2-azido-1*H*-imidazole-4, 5-dicarbonitrile (**3.4**).

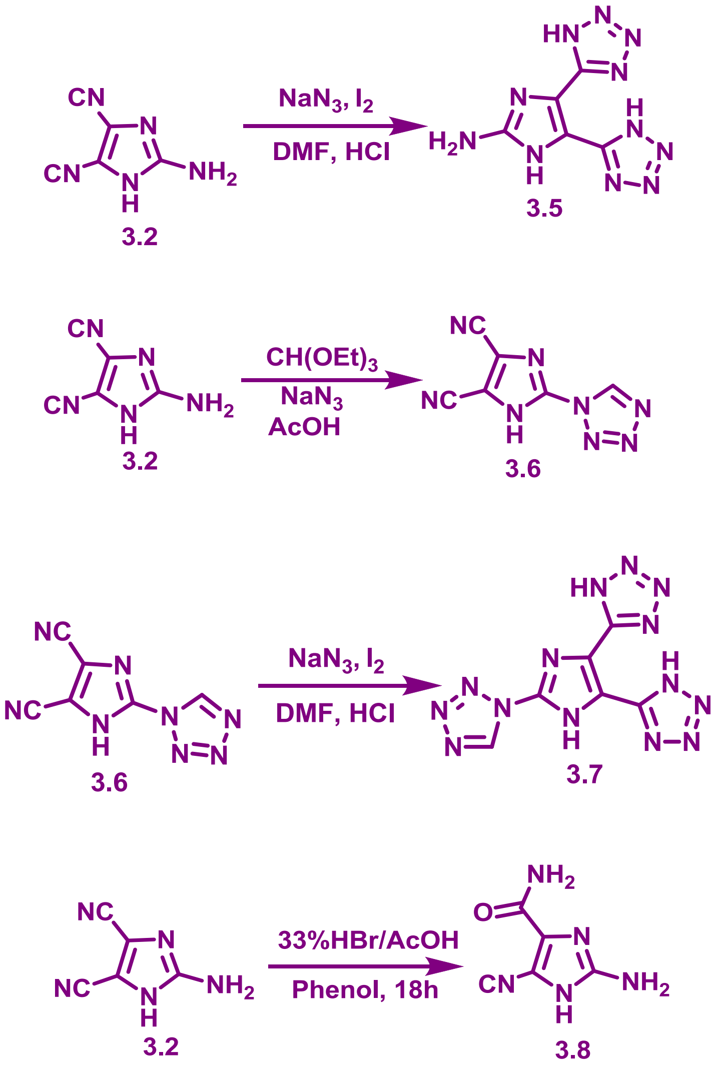


Scheme 3.2. *Conversion of amine to nitro*



Scheme 3.3. *Conversion of amine to azide*

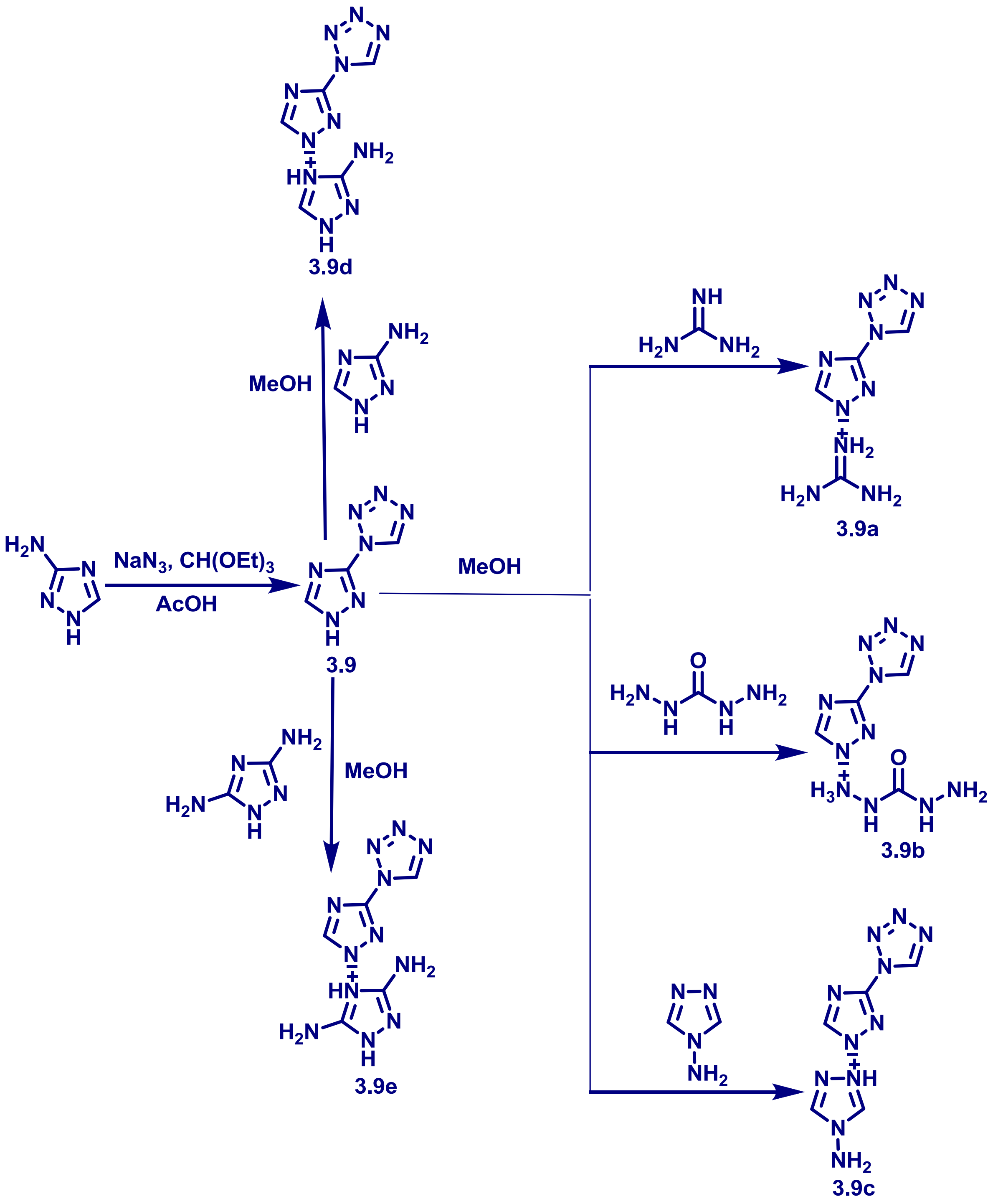
The nitrile groups on imidazole backbone were converted easily to tetrazole rings in high yields using sodium azide and iodine in DMF to obtain 4,5-di(1*H*-tetrazol-5-yl)-1*H*-imidazol-2-amine (**3.5**). **3.2** reacted with triethylorthoformate and sodium azide in acetic acid to produce 2-(1*H*-tetrazol-1-yl)-1*H*-imidazole-4,5-dicarbonitrile (**3.6**) in good yield. The 2-(1*H*-tetrazol-1-yl)-1*H*-imidazole-4,5-dicarbonitrile (**3.6**) reacted with sodium azide and iodine in DMF to obtain 1-[4,5-di(1*H*-tetrazol-5-yl)-1*H*-imidazol-2-yl]-1*H*-tetrazole (**3.7**). **3.2** reacted with triethylorthoformate and sodium azide in acetic acid to produce 2-(1*H*-tetrazol-1-yl)-1*H*-imidazole-4,5-dicarbonitrile **(3.6)** in good yield. To understand the effect of the amide group on energetic properties, we have converted nitrile group to amide in 2-amino-5-cyano-1H-imidazole-4-carboxamide (**3.8**). The nitrile group of **3.8** could not be converted to tetrazole using similar conditions of **3.5** and **3.7**.



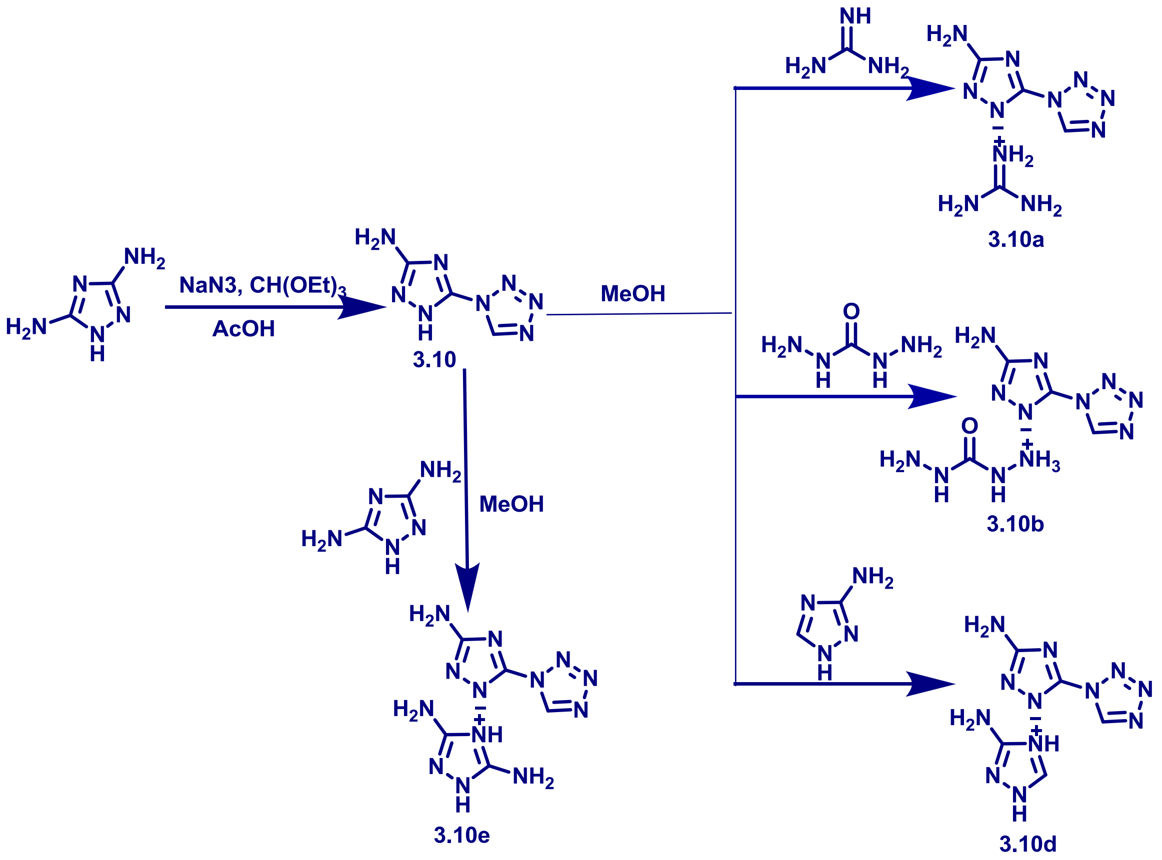
Scheme 3.4. *Formation variety of high nitrogen tetrazole ring systems*

The presence of two or more azole rings is always desirable in energetic backbone to improve its thermal stability and energy content [11]. Moving from imidazole to triazole to tetrazole, improves nitrogen content, heat of formation and oxygen balance. The heats of formation for imidazole, 1,2,4-triazole, and tetrazole are 129, 192 and 326 kJmol^{-1}, respectively [12] and their corresponding nitrogen contents are 41, 61, and 80%. Thus, when 1*H*-1,2,4-triazol-3-amine and 1*H*-1,2,4-triazole-3,5-diamine were reacted with triethylorthoformate and sodiumazide in acetic acid produced 1-(1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole (**3.9**) and 5-(1*H*-tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine (**3.10**), respectively (Schemes 3.5 and 3.6). The reaction of 1*H*-1,2,4-triazole-3,5-diamine with excess triethylorthoformate and sodium azide failed to convert both amino groups to tetrazole rings (**3.13**). **3.10** reacted with tert-butyl nitrite and azidotrimethylsilane to form 1-(3-azido-1*H*-1,2,4-tri- azol-5-yl)-1*H*-tetrazole (**3.11**). 3-Azido-1*H*-1,2,4-triazol-5-amine (**3.12**) was synthesized in excellent yield from 1*H*-1,2,4-triazole-3,5-diamine by following a procedure reported by Kofman and Namestnikov [13] reported using sodium nitrite and sodium azide.

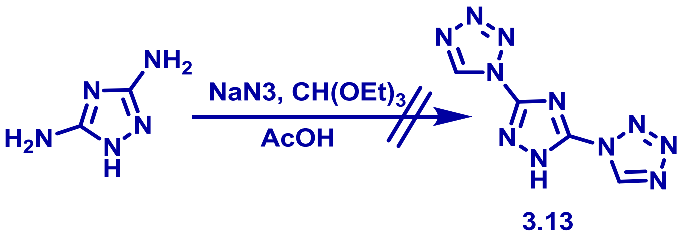
Compound **3.9, 3.10, 3.11** and **3.12** were subsequently deprotonated in alcoholic solution with concomitant formation of salts with various molecules like guanidine, carbohydrazide, 4-amino-4*H*- 1,2,4-triazole, 3-amino-1,2,4-triazole and 3,5-diamino-1,2,4- triazole. The selected cationic moieties are presented in the schemes 3.5 – 3.9. These cationic moieties are well-known due to their energetic properties and widely used in constructing the energetic salts. In chapter 5 Section 5.2.3 we have presented the molecular electrostatic potential graphs to illustrate electrophilicity and nucleophilicity in the selective anionic and cationic moieties [14].



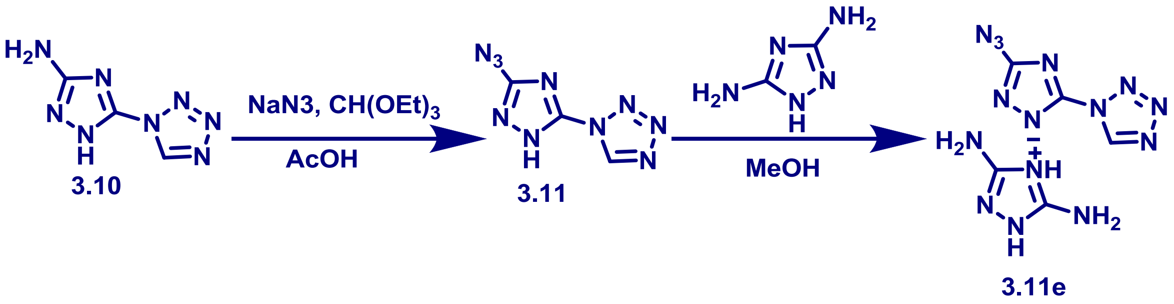
Scheme 3.5. Formation of tetrazole ring from mono amine group and their salts



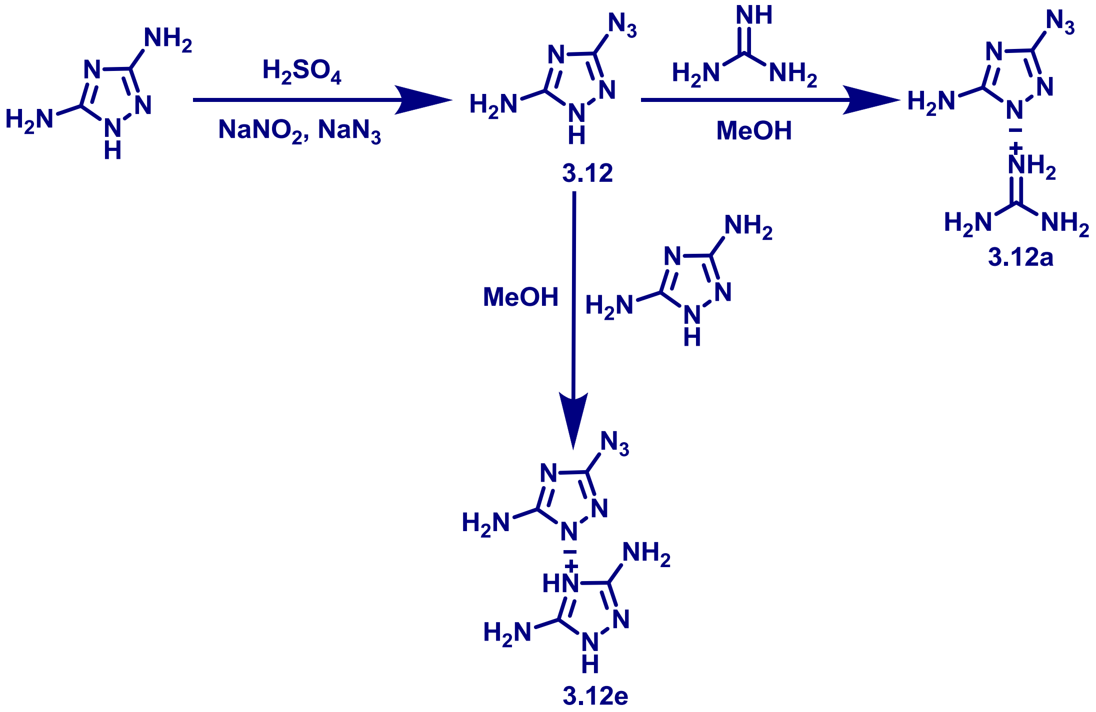
Scheme 3.6. *Formation of tetrazole ring from di amino triazole and their salts*



Scheme 3.7. *Formation of tetrazole ring from mono and di-amine groups*



Scheme 3.8. *Formation of azide from amine group and their salts.*



Scheme 3.9. *Formation of single azide from diamino 1,2,4-triazole and their salts.*

All compounds were characterized by means of elemental analysis, mass spectrometry (MS), IR and NMR (^{1}H and ^{13}C) spectroscopy. As might be expected from the structural similarities between these nitrogen-rich compounds, the vibration modes were also very similar. In most of these azole compounds, the most- important vibrations are the N-H, C-N, C=C and N=N bond stretches. In these compounds, N–H stretching found as an intense absorption at 3100–3500 cm^{-1}, C-N stretching observed in 1000-1300 cm^{-1} and C=C bond stretching in 1600-1700 cm^{-1} region. Compounds containing nitrile group (**3.3, 3.4, 3.6**, and **3.8**) showed C≡N stretching in the 2240-2260 cm^{-1} region. The amide linkage in **3.8** shows C=O stretching at 3096-3447 cm^{-1} and N-H bending at 1577-1616 cm^{-1} region. In the ^{1}H NMR spectra, the proton signals of the anion **3.9** occurred at $\delta \approx 10.12$ and 8.88 ppm, for **3.10** anion, $\delta \approx 9.92$ and 6.65 ppm, for **3.11** anion, $\delta \approx 10.10$ ppm and for **3.12** anion, $\delta \approx 6.27$ ppm and the other signals are assigned to the respective cations. We have also recorded the ^{1}H NMR for **3.10** in D_2O. The proton of the NH (signal at δ 12.63 ppm) and $-NH_2$ group (signal at δ 6.64 ppm) of **3.10** underwent rapid exchange with the protons in D_2O as shown in the ^{1}H NMR spectrum. The signal at δ 9.91 ppm was assigned to the proton of tetrazole ring. No signals were observed in the ^{1}H NMR spectrum that could be assigned to **3.10** supporting the loss of proton(s). Similarly, in the ^{13}C NMR spectra, the three signals of the anion **3.9** observed at δ ≈152, 146 and 143 ppm, for anion **3.10**, three peaks occured at δ ≈157, 150, and 143 ppm, for compound anion **3.11**, signals δ ≈146, 143 and 134 ppm observed and anion **3.12** spectra shows two signals at δ ≈157 and 154 ppm, the remaining signals are associated with the cations. The high resolution mass spectrum of salt **3.9a** exhibited peak at m/z = 197.1009 (M+H) which found in good agreement with its actual mass (m/z = 196.0933). The detailed analysis is presented in experimental section.

3.2.2. Thermal stabilities and energetic properties

The thermal stabilities of all designed compounds were determined by TG-DTA measurements at a heating rate of 10 °C/min. The melting points, thermochemical, and energetic data of designed energetic salts are summarized in Table 3.2. As evident from Table 3.2, compounds **3.5, 3.7, 3.9, 3.10, 3.11** and **3.12** decomposed without melting, and the decomposition temperatures of these compounds are in the range 173 to 238 °C representing good thermal stability. Incorporation of amino group into a triazole ring improves thermal stability as observed in **3.9** and **3.10.** From Table 3.2, the salts of **3.9, 3.10, 3.11** and **3.12** possess lower decomposition temperature as compared to its nonionic compounds. Among **3.9a** to **3.9e** salts **3.9c**, decomposed without melting, and its decomposition temperatures were found above 187 °C. In **3.10a–3.10e, 3.11e** and **3.12a–3.12e** salts, all compounds except **3.10e** decompose without melting. **3.12a–3.12e** salts showed comparable decomposition temperature (~170 °C) to its nonionic azido starting material, **3.12**.

In this work, we have mainly focused on the synthesis and characterization of tetrazole containing energetic materials to improve nitrogen content and their heat of formation. The heat of formation (HOF) is important parameter in evaluating the performance of energetic materials and can be calculated with good accuracy using isodesmic reactions and the lattice energy of salts. The solid state HOF of **3.5, 3.7, 3.9, 3.10, 3.11** and **3.12** were calculated from their gas phase HOF and heat of sublimation and presented in Table 3.1. Calculations were carried out using the Gaussian 03 suite of program [15]. The high positive HOFs of **3.5** and **3.7** clearly reveals the role of tetrazole ring in the improvement of HOF and their HOFs are 602 and 985 kJmol^{-1}, respectively. Similarly, the calculated HOFs of **3.9, 3.10, 3.11** and **3.12** show high positive HOFs. Introduction of tetrazole and azido group on the triazole backbone improves HOF significantly. Comparing **3.9, 3.10** and **3.11** reveals that introduction of amino group in molecular structure reduces the HOF, while insertion of azido group improves HOF. The calculated HOFs of salts are summarized in Table 3.2. All the salts possess high positive HOFs, and salts of **3.11** have highest values due to significant energy contribution from **3.11** anion (610.7 kJmol^{-1}). The calculated values of HOF range from 326– 1032 kJmol^{-1}.

Oxygen balance (OB) is an expression used to indicate the degree, to which an explosive can be oxidized. Owing to the absence of oxygen donor groups in anionic starting materials (**3.5, 3.7, 3.9, 3.10, 3.11** and **3.12**); all of them have negative OB and are in the range from -63 to -91%. The nitrogen content is another very important property in energetic materials. Compounds **3.5, 3.7, 3.9, 3.10, 3.11**, and **3.12** have nitrogen content above 70%, and the salts paired with triazole based cations possess nitrogen content in the range 67 to 75%. One of the most important physical properties of a solid energetic material is its density. The densities of were calculated using the Hofmann approach [16] and the results summarized in Table 3.1. As shown in, the densities of most of the salts range from 1.55 to 1.78 gcm^{-3}. The detonation parameters were calculated by Kamlet-Jacobs equations [17] and Table 3.2 shows that for salts. The calculated detonation pressures (*DP*) were in the range14.7–27.2 GPa, and detonation velocity (*VOD*) were in between 6.0 and 7.85 kms^{-1}, which are more or less close to that of trinitrotoluene (TNT) (P ¼ 19.5 GPa, D ¼ 6.8 kms^{-1}).

Table 3.1. *Energetic properties of nonionic compounds **3.5**, **3.7** and **3.9-3.12**.*

Comd	**[a]NC**	**[b]OB**	**[c]HOF$_{Gas}$**	**[d]HOF$_{Sub}$**	**[e]HOF$_{Solid}$**	**[f]ρ**	**[g]*VOD***	**[h]*DP***	**[i]Q**	**[j]T$_{dc}$**	**[k]Mp**
3.5	70.3	-91.3	749.8	148.0	601.8	1.65	6.33	16.86	780	227	--
3.7	72.1	-82.4	1137.9	152.9	984.9	1.71	6.81	19.97	945	179	--
3.9	71.5	-87.6	559.9	106.0	453.9	1.67	6.68	18.92	910	243	--
3.10	73.7	-84.2	533.9	94.5	439.4	1.65	6.61	18.37	833	238	--
3.11	78.6	-62.9	831.4	98.3	733.1	1.73	7.31	23.16	1045	223	--
3.12	78.4	-70.4	444.8	93.0	351.8	1.61	6.60	18.09	802	173	153

[a]Nitrogen content (%). [b]Oxygen balance (%). [c]Heat of formation in gas phase (kJ/mol). [d]Heat of sublimation (kJmol^{-1}). [e]Heat of formation in solid state (kJmol^{-1}). [f]Density (gcm^{-3}). [g]Velocity of detonation (kms^{-1}). [h]Detonation pressure (GPa). [i]Chemical energy of detonation (calg^{-1}). [j]Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min) (°C). [k]Melting point (°C)

Table 3.2. *Energetic properties of salts of 1-(1H-1,2,4-triazol-3-yl)-1H-tetrazole (**3.9**), 5-(1H-tetrazol-1-yl)-1H-1,2,4-triazol-3-amine (**3.10**), 1-(3-azido-1H-1,2,4-triazol-5-yl)-1H-tetrazole (**3.11**), and 3-azido-1H-1,2,4-triazol-5-amine (**3.12**) salts.*

Compd	**NC (%)**	**[b]OB**	**[c]HOF$_c$**	**[d]HOF$_a$**	**[e]U$_{Pot}$**	**[f]H$_L$**	**[g]HOF$_{salt}$**	**[h]ρ**	**[i]*VOD***	**[j]*DP***	**[k]Q**	**[l]T$_{dec}$**	**[m]Mp**
3.9a	71.4	-98.0	567.2	349.9	522	527	390	1.55	6.07	14.86	696	197	177
3.9b	67.8	-81.1	619.5	349.9	503	508	462	1.58	6.76	18.70	907	186	143
3.9c	69.7	-97.7	946.9	349.9	508	513	784	1.59	6.66	18.24	1019	187	--
3.9d	69.7	-97.7	796.4	349.9	508	513	634	1.59	6.38	16.72	856	191	174
3.9e	71.1	-94.9	753.8	349.9	497	502	601	1.59	6.32	16.37	792	194	141
3.10a	73.0	-94.8	567.2	368.1	510	515	420	1.55	6.15	15.26	706	200	--
3.10b	69.4	-79.3	619.5	368.1	493	498	490	1.58	6.79	18.83	901	195	--
3.10d	71.2	-94.9	796.4	368.1	497	502	662	1.59	6.43	16.99	854	190	--
3.10e	72.5	-92.4	753.8	368.1	488	493	629	1.58	6.37	16.62	792	200	120
3.11e	75.8	-78.0	753.8	610.7	481	486	878	1.67	6.86	19.94	894	203	--
3.12a	76.1	-87.0	567.2	296.6	533	538	326	1.56	6.20	15.55	659	167	--
3.12e	75.0	-85.7	753.8	296.6	506	511	539	1.60	6.46	17.18	768	172	--

[a]Nitrogen Content (%). [b]Oxygen balance (%). [c]Heat of formation of cation (kJ/mol). [d]Heat of formation of anion (kJ/mol). [e]Lattice potential energy (kJmol^{-1}). [f]Lattice energy (kJmol^{-1}). [g]Heat of formation of salt (kJmol^{-1}). [h]Density (gcm^{-3}). [i]Velocity of detonation (kms^{-1}). [j]Detonation pressure (GPa). [k]Chemical energy of detonation (calg^{-1}). [l]Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [m]Melting point (°C

3.3. Summary

A family of nitrogen-rich compounds and energetic salts were prepared and fully characterized. The densities of the designed salts fall within the range 1.55 to 1.78 g/cm^3, which place most of them in a class of relatively dense compounds. Using Kamlet–Jacobs equations, we calculated their detonation pressures and velocities; these fall in the range 14.7 to 27.2 GPa and 6.0–7.85 kms^{-1}, respectively. Salts of 3-nitro-1,2,4-triazole cation show high positive heat of formation, density and performance. All salts decompose between 146 to 238 °C and own good thermal stability. All the designed compounds possess negative oxygen balance, thus affects the performance of these compounds, which needs external oxygen supplier for the conversion of explosives into their gaseous reaction products. We are currently working on the mixture of these compounds with suitable oxidizer to evaluate their performance and to expand the scope of these compounds to the construction of nitrogen-rich frameworks containing diverse nitrogen heterocyclic building blocks. More importantly, it is noteworthy that most of the compounds in this work amenable to large scale synthesis with high yields, easy to control reaction conditions, reproducibility and facile purification. Furthermore, based on detonation properties and superior thermal stabilities, these salts have potential as gas generators and enthalpy modifiers in energetic materials.

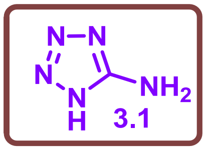
3.4. Experimental section

3.4.1. Materials and instruments

The reagents were available commercially and were used as purchased without further purification. Reactions were monitored by TLC analysis, by using precoated silica gel TLC plates obtained from Merck. ^{1}H and ^{13}C NMR spectroscopic data were recorded on a Bruker Avance 400 MHz FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard and [D6] DMSO as the solvent. Mass analysis was performed on a LC-MS spectrometer. Melting points and decomposition temperatures were determined by DSC-TGA using TA instruments SDT Q 600 instrument. The IR spectra were recorded on a Perkin-Elmer IR spectrometer by using KBr pellets. The HRMS were recorded on a Bruker Maxis instrument. Elemental analyses were performed on a fash EA 1112 full automatic trace element analyzer.

3.4.2. Synthetic procedures

***1H-Tetrazol-5-amine* (*3.1*)**: A mixture of cyanamide (0.200 g, 4.76 mmol), sodium azide (0.309 g, 4.76 mmol) and iodine (0.06 g) suspended in DMF (10 mL), was refluxed for 6h with stirring. The reaction mixture was cooled to room temperature and hydrochloric acid (10 mL, 1 M) was added. The reaction mixture was extracted with ethyl acetate and dried over sodium sulfate. The solvent was removed under reduced pressure and the products were isolated with satisfactory purity as a white solid (0.280 g, 69.2 % yield).



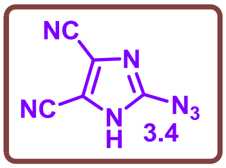
IR (KBr pellet, ν_{max}/cm^{-1}) : 3410, 3217, 2934, 2812, 2501, 2199, 1658, 1568, 1516, 1415, 1253, 1105, 1051, 1012, 923, 653, 621.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 4.97 (s, 4H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 164.

Mass : 86.00.

***2-Azido-1H-imidazole-4,5-dicarbonitrile* (*3.4*)**: 2-Amino-1*H*-imidazole-4,5-dicarbonitrile (1.33 g, 10 mmol) dissolved in hydrochloric acid (7.5 mL) in a 100 mL round-bottom flask was cooled to ~0°C in an ice bath. To this stirred mixture, $NaNO_2$ (1 g, 40 mmol) in 3 mL of water was added and stirred vigorously at room temperature. After this, excess amount of $NaNO_2$ was added slowly to the mixture (up to disappearing starting material spot in TLC). The crude product was extracted with ethyl acetate and the solvent was evaporated under vacuum to give the yellow solid (0.110 g, 69.1 % yield). DSC-TGA (10 °C min^{-1}): 114 °C (m.p.), 178 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3308, 2924, 2854, 2446, 2361, 2239, 2156, 1712, 1562, 1525, 1482, 1442, 1410, 1315, 1228, 1140, 719, 652.

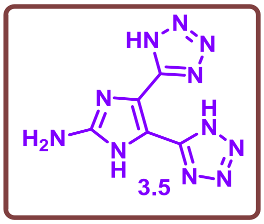
^{13}C NMR (100MHz, DMSO) : δ (ppm) 150.2, 117.2, 115.2.

Mass : 160.00.

Anal. Calcd. for C_5HN_7 : C, 37.74; H, 0.63; N, 61.62.

Found : C, 37.62; H, 0.71; N, 61.52.

***4,5-Di(1H-tetrazol-5-yl)-1H-imidazol-2-amine* (3.5):** Sodium azide (0.395 g, 6 mmol) and iodine (0.06 g, 0.47 mmol) was added to a solution of 2-amino-1*H*-imidazole-4,5-dicarbonitrile (0.266 g, 2 mmol) in DMF (10 mL). The reaction mixture was refluxed for 6h with stirring. The reaction mixture was cooled to room temperature and added hydrochloric acid (10 mL, 1M). The reaction mixture was extracted with ethyl acetate. The crude product was purified by column chromatography over silica gel with n-hexane/EtOAc and dried over sodium sulfate. The solvent was removed under reduced pressure and the product was isolated with satisfactory purity as orange solid (0.225 g, 51.3 % yield). DSC-TGA (10 °C min^{-1}): 265 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3136, 2934, 2241, 2150, 1651, 1523, 1437, 1388, 1344, 1307, 1251, 1197, 667, 642, 505.

^{1}H NMR (400 MHz, DMSO) : *δ* (ppm) 7.21 (s, 2H).

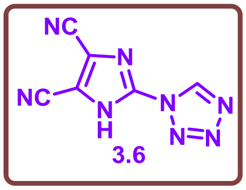
^{13}C NMR (100MHz, DMSO) : δ (ppm) 162.7, 153.8, 142.3.

Mass : 220.1048.

Anal. Calcd. for $C_5H_5N_{11}$: C, 27.40; H, 2.30; N, 70.30.

Found : C, 27.51; H, 2.36; N, 70.21.

***2-(1H-Tetrazol-1-yl)-1H-imidazole-4,5-dicarbonitrile* (3.6):** 2-Amino-1*H*-imidazole-4,5-dicarbonitrile (1 g, 7.5 mmol) and sodium azide (0.733 g, 11.27 mmol) was suspended in triethyl orthoformate (2 mL) and glacial acetic acid (20 mL) was added, and the mixture was refluxed for 8 hrs. The slurry was concentrated in vacuum, and residue was partitioned between ethyl acetate (250 mL) and 3N HCl (50 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum to get the compound as a white solid (0.900 g, 64.5 % yield). DSC-TGA (10 °C min^{-1}): 238 °C (dec).



3.6

IR (KBr pellet, ν_{max}/cm^{-1}) : 3439, 3350, 2922, 2852, 2233, 1693, 1651, 1591, 1531, 1469, 1309, 1255, 1143, 1103, 1028, 866, 798, 715, 652.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.89 (s, 1H).

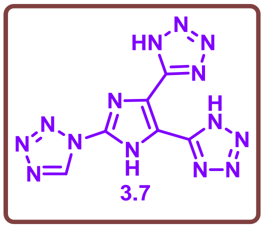
^{13}C NMR (100MHz, DMSO) : *δ* (ppm) 153.8, 142.7, 115.3, 112.5.

Mass : 187.0476.

Anal. Calcd. for $C_6H_2N_8$: C, 38.72; H, 1.08; N, 60.20.

Found : C, 38.65; H, 1.16; N, 60.36.

***5,5'-(2-(1H-Tetrazol-1-yl)-1H-imidazole-4,5-diyl)bis(1H-tetrazole)* (*3.7*):** Sodium azide (0.172 g, 2.65 mmol) and iodine (0.120 g, 47.2 mmol) were added to a solution of 2-(1*H*-tetrazol-1-yl)-1*H*-imidazole-4,5-dicarbonitrile (0.215 g, 1.1 mmol) in DMF (10 mL). The reaction mixture was refluxed for 6h with stirring. The reaction mixture was cooled to room temperature and added hydrochloric acid (20 mL, 1M). The reaction mixture was extracted with ethyl acetate.The crude product was purified by column chromatography over silica gel with n-hexane/EtOAc and dried over sodium sulfate. The solvent was removed under reduced pressure and the product was isolated with satisfactory purity as a white solid (0.060 g, 15% yield). DSC-TGA (10 °C min^{-1}): 179 °C (dec).



3.7

IR (KBr pellet, ν_{max}/cm^{-1}) : 3324, 3136, 2934, 2241, 2150, 1651, 1523, 1437, 1388, 1344, 1307, 1251, 1197, 667, 642, 505.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.89 (s, 1H).

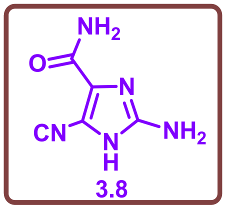
^{13}C NMR (100MHz, DMSO) : δ (ppm) 160.5, 153.9, 146.3, 142.1.

Mass : 273.0707.

Anal. Calcd. for $C_6H_4N_{14}$: C, 26.48; H, 1.48; N, 72.04.

Found : C, 26.35; H, 1.41; N, 72.15.

2-Amino-5-cyano-1H-imidazole-4-carboxamide ***(3.8)***: 2-Amino-1*H*-imidazole-4,5-dicarbonitrile (0.300 g, 2.25 mmol) was added to the mixture of phenol (0.848 g, 9.02 mmol) and 33% HBr/AcOH. The reaction mixture was stirred for 18h at room temperature. Then, the reaction mixture was poured into diethyl ether (20 mL) and the precipitate was filtered. The collected solid was dissolved in minimal amount of refluxed methanol (5 mL) and cooled to room temperature followed by drop wise addition of diethyl ether, the precipitate filtered and dried. White solid (0.250 g, 73.5 % yield). DSC-TGA (10 °C min^{-1}): 180 °C (m.p.).

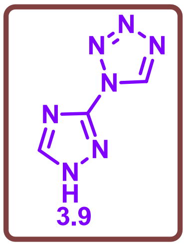


3.8

IR (KBr pellet, ν_{max}/cm^{-1}) : 3447, 3406, 3348, 3096, 2878, 2737, 2233, 1705, 1670, 1616, 1595, 1577, 1508, 1452, 1396, 1359, 1251, 1213, 1070, 1043, 783, 702, 657, 601, 545, 486, 455.

^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 7.93 (s, 2H), 7.69 (s, 2H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 158.36, 149.32, 133.32, 111.94, 102.55.
Mass	: 152.0571.
Anal. Calcd. for $C_5H_5N_5O$	: C, 39.74; H, 3.33; N, 46.34.
Found	: C, 39.62; H, 3.38; N, 46.23.

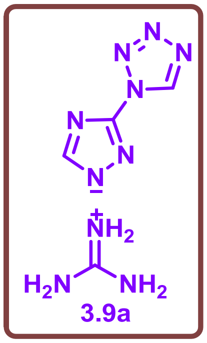
***1-(1H-1,2,4-Triazol-3-yl)-1H-tetrazole* (*3.9*):** 1*H*-1,2,4-triazol-3-amine (1 g, 11.90 mmol) and sodium azide (0.773 g, 23.80 mmol) was suspended in triethyl orthoformate (3 mL) and glacial acetic acid (20 mL) was added, and the mixture was refluxed for 8h. The slurry was concentrated in vacuum and residue was partitioned between ethyl acetate (200 mL) and 3N HCl (100 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum to get the target compound as white solid (1.5 g, 91.9 % yield). DSC-TGA (10 °C min^{-1}): 228 °C (dec).



3.9

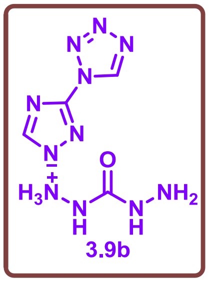
IR (KBr pellet, ν_{max}/cm^{-1})	: 3130, 3032, 2985, 2908, 1547, 1479, 1381, 1324, 1277, 1200, 1179, 1122, 1091, 1014, 977.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 10.12 (s, 1H), 8.88 (s, 1H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 152.9, 146.2, 143.5.
Mass	: 160.0345.
Anal. Calcd. for $C_3H_3N_7$	: C, 26.28; H, 2.21; N, 71.51.
Found	: C, 26.58; H, 1.42; N, 72.21.

***Diaminomethaniminium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.9a*):** A solution of guanidine (0.089 g, 0.729 mmol) was slowly added to a solution of 1-(1*H*-1,2,4-Triazol-3-yl)-1*H*-tetrazole (0.100 g, 0.729 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.135 g, 94.4 % yield). DSC-TGA (10 °C min^{-1}): 177 °C (m.p.), 197 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1})	: 3410, 3192, 3146, 3032, 2980, 2908, 1676, 1578, 1541, 1479, 1386, 1272, 1189, 1112, 1091, 972, 962, 827, 539.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 8.05 (s, 1H), 6.82 (s, 1H) 4.91 (s, 6H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 158.3, 152.9, 146.2, 143.5.
Mass	: 196.0933.
Anal. Calcd. for $C_4H_8N_{10}$	: C, 24.49; H, 4.11; N, 71.40.
Found	: C, 24.56; H, 4.06; N, 71.52.

***(Hydrazinylcarbonyl) hydrazinium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.9b*):** A solution of carbohydrazide (0.065 g, 0.7293 mmol) was slowly added to a solution of 1-(1*H*-1,2,4-Triazol-3-yl)-1*H*-tetrazole (0.100 g, 0.729 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.150 g, 90.5 % yield). DSC-TGA (10 °C min^{-1}): 143 °C (m.p.), 186 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1})	: 3368, 3306, 3140, 3037, 2985, 2913, 1635, 1552, 1479, 1469, 1381, 1319, 1267, 1200, 1122, 1091, 1019, 982.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.45 (s, 1H), 8.19 (s, 1H) 6.57 (s, 2H), 5.74 (s, 5H).

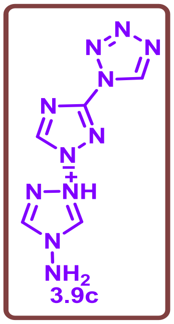
^{13}C NMR (100MHz, DMSO) : δ (ppm) 167.1, 157.6, 151.2, 151.1, 148.3.

Mass : 228.

Anal. Calcd. for $C_4H_9N_{11}O$: C, 21.15; H, 3.99; N, 67.82; O, 7.04.

Found : C, 21.06; H, 3.91; N, 67.62.

***4-Amino-4H-1,2,4-triazol-1-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.9c*):** A solution of 4*H*-1,2,4-triazol-4-amine (0.061 g, 0.729 mmol) was slowly added to a solution of 1-(1*H*-1,2,4-Triazol-3-yl)-1*H*-tetrazole (0.100 g, 0.729 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product.White solid (0.150 g, 93 % yield). DSC-TGA (10 °C min^{-1}): 187 °C (dec).



3.9c

IR (KBr pellet, ν_{max}/cm^{-1}) : 3130, 3027, 2908, 1878, 1831, 1626, 1547, 1484, 1459, 1391, 1272, 1189, 1122, 1096, 1024, 982, 832, 729.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 10.12 (s, 1H), 8.88 (s, 1H) 8.41 (s, 2H), 6.23 (s, 3H).

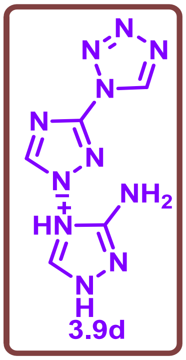
^{13}C NMR (100MHz, DMSO) : δ (ppm) 152.9, 146.2, 144.6, 143.5.

Mass : 222.

Anal. Calcd. for $C_5H_7N_{11}$: C, 27.15; H, 3.19; N, 69.66.

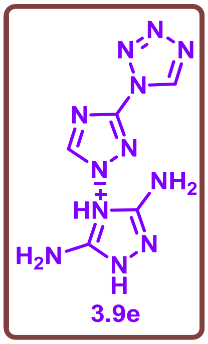
Found : C, 27.06; H, 3.25; N, 69.51.

***3-Amino-1H-1,2,4-triazol-4-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.9d*):** A solution of 3-amino-1,2,4-triazole (0.060 g, 0.729 mmol) was slowly added to a solution of 1-(1*H*-1,2,4-Triazol-3-yl)-1*H*-tetrazole (0.100 g, 0.729 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.160 g, 99.2 % yield). DSC-TGA (10 °C min^{-1}): 174 °C (m.p.), 191 °C (dec).


3.9d

IR (KBr pellet, ν_{max}/cm^{-1})	: 3399, 3311, 3125, 3037, 2985, 2918, 1624, 1547, 1479, 1417, 1319, 1283, 1189, 1127, 1091, 1055, 1008, 982.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 10.13 (s, 1H), 8.88 (s, 2H) 5.50 (s, 2H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 158.8, 152.9, 146.3, 143.5.
Mass	: 222.
Anal. Calcd. for $C_5H_7N_{11}$	: C, 27.15; H, 3.19; N, 69.66.
Found	: C, 27.06; H, 3.24; N, 69.52.

***3,5-Diamino-1H-1,2,4-triazol-4-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.9e*):** A solution of 3,5-diamino-1,2,4-triazole (0.072 g, 0.729 mmol) was slowly added to a solution of 1-(1*H*-1,2,4-Triazol-3-yl)-1*H*-tetrazole (0.100 g, 0.729 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.155 g, 90 % yield). DSC-TGA (10 °C min^{-1}): 141 °C (m.p.), 194 °C (dec).



3.9e

IR (KBr pellet, ν_{max}/cm^{-1}) : 3410, 3327, 3130, 3037, 2985, 2918, 2721, 1883, 1831, 1650, 1541, 1474, 1391, 1283, 1117, 1086, 1034, 972.

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 10.13 (s, 1H), 8.88 (s, 1H).

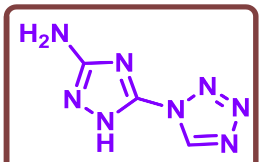
^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 158.3, 152.9, 148.1, 146.2, 143.5.

Mass : 237.

Anal. Calcd. for $C_5H_8N_{12}$: C, 25.43; H, 3.41; N, 71.16.

Found : C, 25.51; H, 3.36; N, 71.32.

***5-(1H-Tetrazol-1-yl)-1H-1,2,4-triazol-3-amine* (*3.10*):** 1*H*-1,2,4-triazole-3,5-diamine (1 g, 10.1 mmol) and sodium azide (1.969 g, 30.3 mmol) was suspended in triethyl orthoformate (8 mL) and glacial acetic acid (35 mL) was added, the mixture was reflexed for 8h. The slurry was concentrated in vacuum and residue was partitioned between ethyl acetate (500 mL) and 3N HCl (100 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum to get the compound as white solid (0.800 g, 52.1 % yield). DSC-TGA (10 °C min^{-1}): 238 °C (dec).

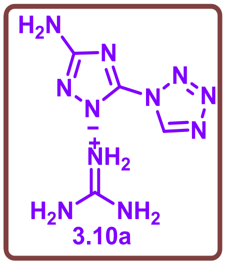


3.10

IR (KBr pellet, ν_{max}/cm^{-1}) : 3491, 3393, 3119, 2922, 1697, 1651, 1562, 1531, 1444, 1325, 1255, 1192, 1163, 1101, 1072, 1039, 978, 798, 733, 653, 526.

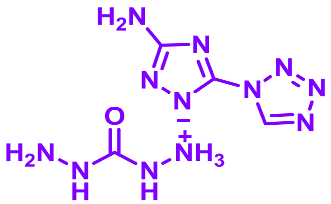
^{1}H NMR (400 MHz, CD_3OD)	: δ (ppm) 12.64 (s, 1H), 9.92 (s, 1H) 6.65 (s, 2H).
^{13}C NMR (100MHz, CD_3OD)	: δ (ppm) 157.9, 150.4, 143.0.
Mass	: 153.0361.
Anal. Calcd. for $C_3H_4N_8$	: C, 23.69; H, 2.65; N, 73.66.
Found	: C, 23.76; H, 2.58; N, 73.45.

Diaminomethaniminium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide **(*3.10a*):** A solution of guanidine (0.080g, 0.6578 mmol), was slowly added to a solution of 5-(1*H*-Tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.130 g, 93.6 % yield). DSC-TGA (10 °C min^{-1}): 200 °C (dec 1), 268 °C (dec 2).


3.10a

IR (KBr pellet, ν_{max}/cm^{-1})	: 3112, 2980, 1961, 1605, 1479, 1419, 1200, 1063, 953.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 9.91 (s, 1H), 6.94 (s, 6H) 6.64 (s, 2H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 158.3, 157.9, 150.4, 143.0.
Mass	: 212.1118.
Anal. Calcd. for $C_4H_9N_{11}$	: C, 22.75; H, 4.30; N, 72.96.
Found	: C, 22.61; H, 4.41; N, 72.85.

(Hydrazinylcarbonyl)hydrazonium 3-mino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide **(*3.10b*):** A solution of carbohydrazide (0.059 g, 0.6578 mmol), was slowly added to a solution of 5-(1*H*-Tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.150 g, 94.2 % yield). DSC-TGA (10 °C min^{-1}): 195 °C (dec).



3.10b

IR (KBr pellet, ν_{max}/cm^{-1}) : 3358, 3325, 3298, 3199, 1659, 1517, 1445, 1319, 1265, 1204, 1100, 1051, 980, 919.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.94 (s, 1H), 7.25 (s, 5H) 6.68 (s, 2H).

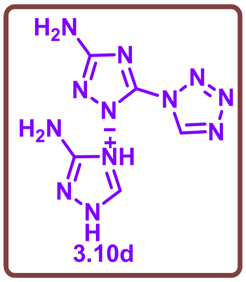
^{13}C NMR (100MHz, DMSO) : δ (ppm) 162.2, 157.9, 150.4, 143.0.

Mass : 243.1173.

Anal. Calcd. for $C_4H_{10}N_{12}O$: C, 19.84; H, 4.16; N, 69.40.

Found : C, 19.69; H, 4.23; N, 69.28.

***3-Amino-1H-1,2,4-triazol-4-ium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.10d*):** A solution of 3-amino-1,2,4-triazole (0.066 g, 0.6578 mmol), was slowly added to a solution of 5-(1*H*-Tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.150 g, 96.6 % yield). DSC-TGA (10 °C min^{-1}): 190 °C (dec).



3.10d

IR (KBr pellet, ν_{max}/cm^{-1}) : 3472, 3360, 3126, 1651, 1558, 1531, 1448, 1421, 1377, 1325, 1257, 1194, 1072, 979, 868, 731, 650, 621.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.90 (s, 1H), 8.42 (s, 4H) 6.67 (s, 2H).

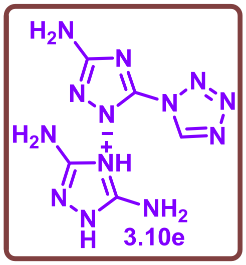
^{13}C NMR (100MHz, DMSO) : δ (ppm) 157.91, 150.45, 144.62, 143.02.

Mass : 237.

Anal. Calcd. for $C_5H_8N_{12}$: C, 25.43; H, 3.41; N, 71.16.

Found : C, 25.15; H, 3.76; N, 70.69.

***3,5-Diamino-1H-1,2,4-triazol-4-ium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.10e*):** A solution of 3,5-diamino-1,2,4-triazole (0.065 g, 0.6578 mmol), was slowly added to a solution of 5-(1*H*-Tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.160 g, 96.8 % yield). DSC-TGA (10 °C min^{-1}): 120 °C (m.p.), 200 °C (dec).



3.10e

IR (KBr pellet, ν_{max}/cm^{-1}) : 3395, 3304, 3112, 1648, 1562, 1516, 1486, 1410, 1263, 1091, 1055, 974.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.91 (s, 1H), 6.67 (s, 2H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 157.9, 150.4, 143.1, 143.0.

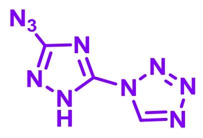
Mass : 251.

Anal. Calcd. for $C_5H_9N_{13}$: C, 23.91; H, 3.61; N, 72.48.

Found : C, 24.12; H, 3.21; N, 72.65.

***1-(3-Azido-1H-1,2,4-triazol-5-yl)-1H-tetrazole* (*3.11*):** In 25 mL round-bottom flask, 5-(1*H*-tetrazol-1-yl)-1H-1,2,4-triazol-3-amine (0.200 g, 1.31 mmol) was dissolved in CH_3CN (4 mL) and cooled to 0°C in an ice bath. To this stirred mixture t-BuONO (0.203 g, 0.2347 μL, 2.27

mmol) was added followed by $TMSN_3$ (0.1818 g, 0.2075 µL, 1.8 mmol) dropwise. The resulting solution was stirred at room temperature for 1h. The reaction mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography (hexane) to give the target product as a orange solid (0.200 g, 85.3 % yield). DSC-TGA (10 °C min^{-1}): 223 °C (dec).



3.11

IR (KBr pellet, ν_{max}/cm^{-1}) : 3264, 3117, 2155, 1699, 1633, 1532, 1374, 1319, 1253, 1177, 1086, 974, 878, 726.

^1H NMR (400 MHz, DMSO) : δ (ppm) 10.14 (s, 1H).

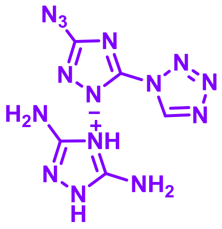
^{13}C NMR (100MHz, DMSO) : δ (ppm) 146.2, 143.6, 134.4.

Mass : 179.0547.

Anal. Calcd. for $C_3H_2N_{10}$: C, 20.23; H, 1.13; N, 78.64.

Found : C, 20.32; H, 1.18; N, 78.54.

***3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* (*3.11e*):** A solution of 3,5-diamino-1,2,4-triazole (0.112 g, 1.13 mmol), was slowly added to a solution of 1-(3-Azido-1*H*-1,2,4-triazol-5-yl)-1*H*-tetrazole (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.280 g, 88.9 % yield). DSC-TGA (10 °C min^{-1}): 203 °C (dec).



3.11e

IR (KBr pellet, ν_{max}/cm^{-1}) : 3399, 3311, 3104, 2136, 1707, 1655, 1629, 1562, 1479, 1422, 1262, 1086, 1055, 977.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 10.11 (s, 1H).

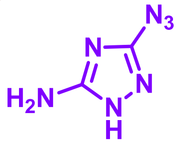
^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.9, 153.1, 150.3, 143.2.

Mass : 278.

Anal. Calcd. for $C_5H_7N_{15}$: C, 21.66; H, 2.55; N, 75.79.

Found : C, 21.52; H, 2.58; N, 75.63.

***3-Azido-1H-1,2,4-triazol-5-amine* (*3.12*):** 1*H*-1,2,4-Triazole-3,5-diamine (1.5 g, 12 mmol) was dissolved in sulfuric acid (15 mL of 20%) at room temp. The clear solution obtained after dissolution was cooled to ~0-5 °C and a solution of sodium nitrite (0.166 g, 24 mmol) in water (20 mL) was added slowly to this solution over a period of 2h keeping the temperature below 10 °C. A small amount of urea was added to the bright yellow reaction mixture to expel the oxides of nitrogen. A solution of sodium azide (0.156 g, 24 mmol) in water (20 mL) was added in small portions while keeping the temperature below 10 °C. The resulting solution was stirred for 1h at 20 °C and afterwards slowly heated to 40 °C. The solution was neutralized using sodium hydrogen carbonate and the product was extracted using ethyl acetate. The combined extracts were dried over magnesium sulfate. The crude off-white product, isolated by removing the solvent under vacuum, was recrystallized from dry toluene to obtain as a white solid (1.4 g, 93.3 % yield). DSC-TGA (10 °C min^{-1}): 153 °C (m.p.), 173 °C (dec).



3.12

IR (KBr pellet, ν_{max}/cm^{-1}) : 3470, 3430, 3470, 3336, 3128, 2142 (N_3), 1660, 1435, 1221, 1019, 816.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 11.84 (s, 1H), 6.27 (s, 2H).

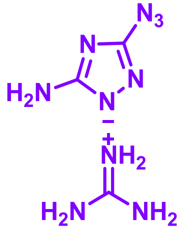
^{13}C NMR (100MHz, DMSO) : δ (ppm) 157.4, 154.

Mass : 148.0348.

Anal. Calcd. for $C_2H_3N_7$: C, 19.20; H, 2.42; N, 78.38.

Found : C, 19.12; H, 2.46; N, 78.21.

***Diaminomethaniminium 5-amino-3-azido-1,2,4-triazol-1-ide* (*3.12a*):** A solution of guanidine (0.047 g, 0.8 mmol), was slowly added to a solution of 3-Azido-1*H*-1,2,4-triazol-5-amine (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.132 g, 89.6 % yield). DSC-TGA (10 °C min^{-1}): 167 °C (dec).



3.12a

IR (KBr pellet, ν_{max}/cm^{-1}) : 3408, 3200, 2147 (N_3), 1665, 1605, 1578, 1545, 1358, 1227, 1008.

^1H NMR (400 MHz, DMSO) : δ (ppm) 6.93 (s, 6H), 6.28 (s, 2H).

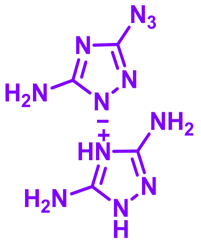
^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.3, 157.4, 154.4.

Mass : 185.

Anal. Calcd. for $C_3H_8N_{10}$: C, 19.57; H, 4.38; N, 76.06.

Found : C, 19.46; H, 4.31; N, 76.21.

***3,5-Diamino-1H-1,2,4-triazol-4-ium 5-amino-3-azido-1,2,4-triazol-1-ide* (*3.12e*):** A solution of 3,5-diamino-1,2,4-triazole (0.079 g, 0.8 mmol), was slowly added to a solution of 3-Azido-1*H*-1,2,4-triazol-5-amine (0.100 g, 0.6535 mmol) in methanol (8 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.170 g, 94.8 % yield). DSC-TGA (10 °C min^{-1}): 172 °C (dec).



3.12e

IR (KBr pellet, ν_{max}/cm^{-1}) : 3408, 3315, 3117, 2147(N3), 1621, 1561, 1490, 1419, 1347, 1221, 1052.

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 6.28 (s, 2H), 5.14 (s, 4H).

^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 158.8, 157.4, 154.4, 153.2.

Mass : 225.1073.

Anal. Calcd. for $C_4H_8N_{12}$: C, 21.43; H, 3.60; N, 74.97.

Found : C, 21.37; H, 3.65; N, 74.85.

3.5. References

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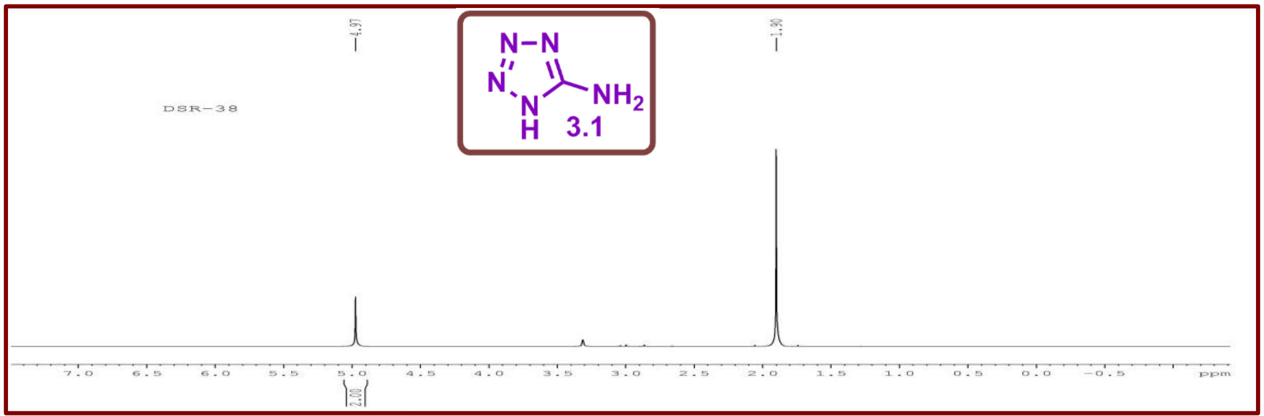


Figure 2.S1 *^{1}H NMR spectrum of 1H-Tetrazol-5-amine* ***(3.1)***

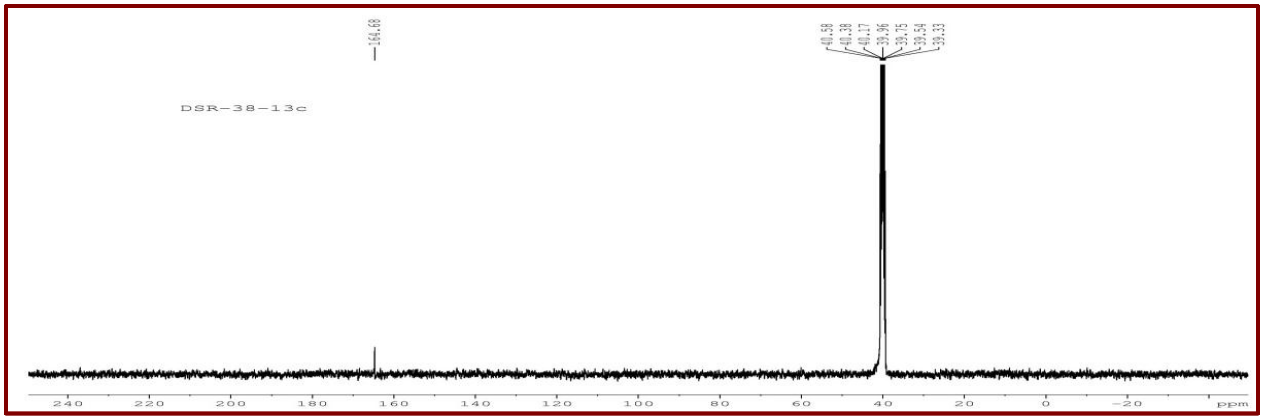


Figure 2.S2 *^{13}C NMR spectrum of 1H-Tetrazol-5-amine* ***(3.1)***

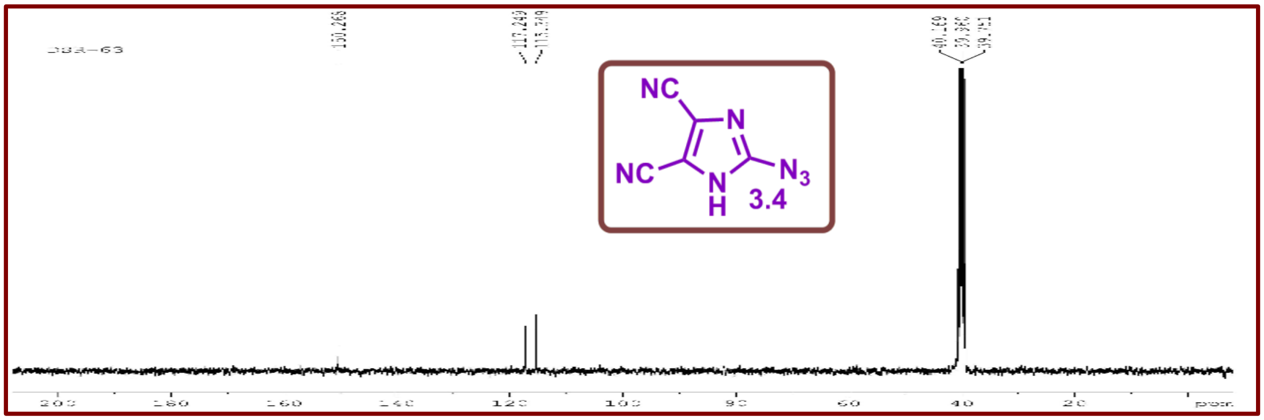


Figure 2.S3 ^{13}C NMR spectrum of 2-Azido-1H-imidazole-4,5-dicarbonitrile ***(3.4)***

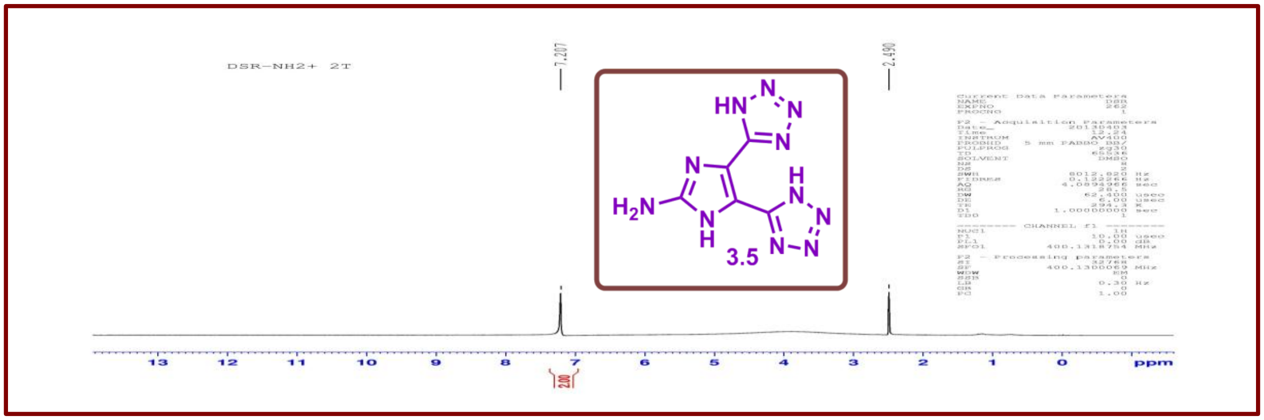


Figure 2.S4 ^{1}*H NMR spectrum of 4,5-Di(1H-tetrazol-5-yl)-1H-imidazol-2-amine*(**3.5**)

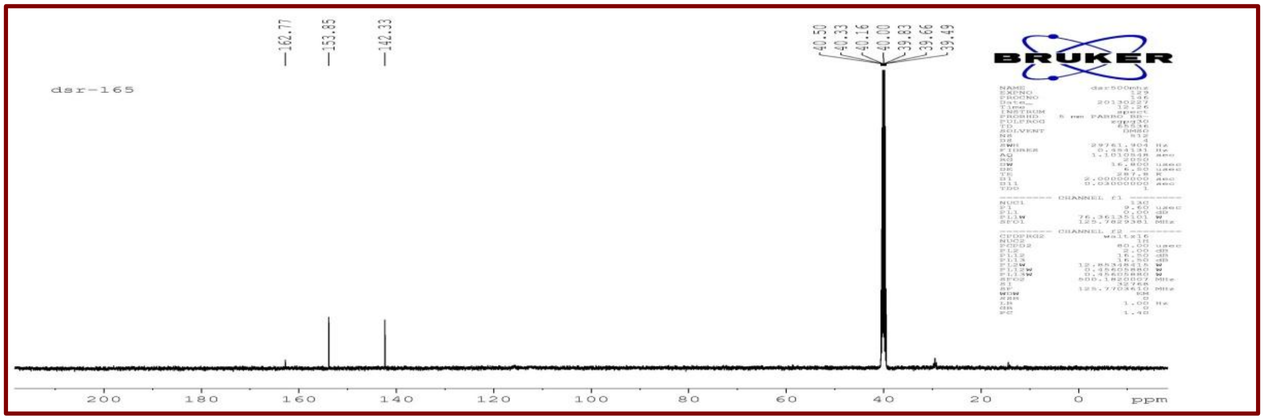


Figure 2.S5 ^{13}*C NMR spectrum of 4,5-Di(1H-tetrazol-5-yl)-1H-imidazol-2-amine*(**3.5**)

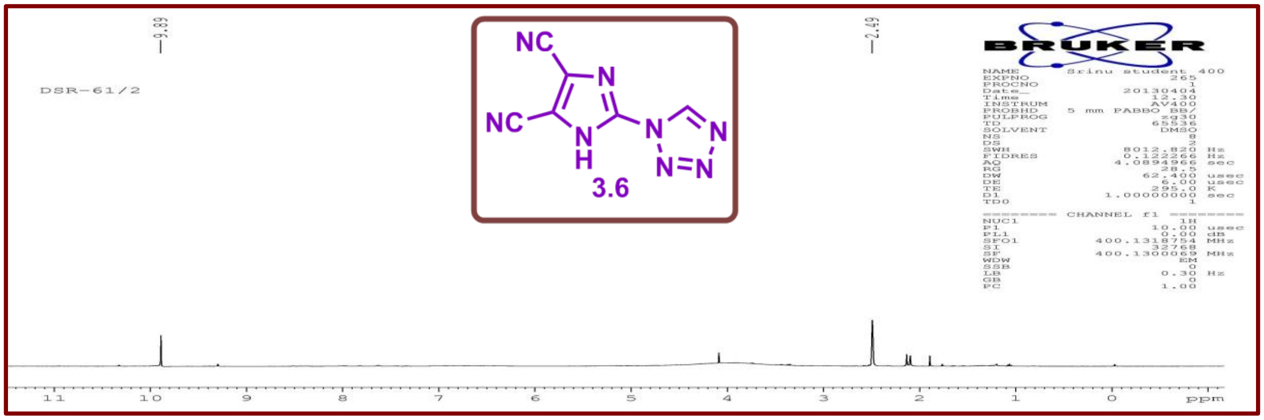


Figure 2.S6 ^{1}*H NMR spectrum of 2-(1H-Tetrazol-1-yl)-1H-imidazole-4,5-dicarbonitrile*(**3.6**)

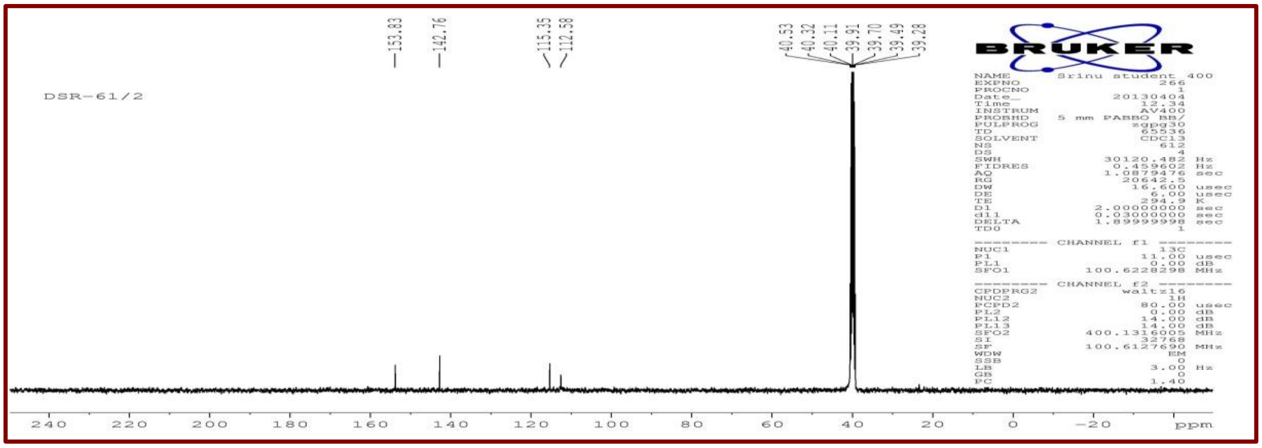


Figure 2.S7 ^{13}*C NMR spectrum of 2-(1H-Tetrazol-1-yl)-1H-imidazole-4,5-dicarbonitrile****(3.6)***

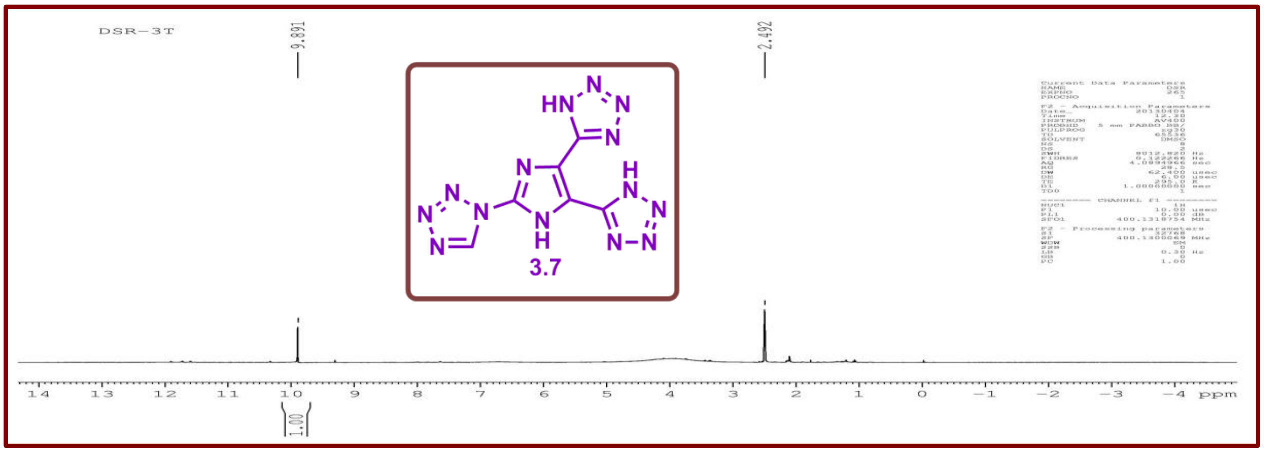


Figure 2.S8 ^{1}*H NMR spectrum of 5, 5'-(2-(1H-Tetrazol-1-yl)-1H-imidazole-4,5-diyl)bis(1H-tetrazole)* ***(3.7)***

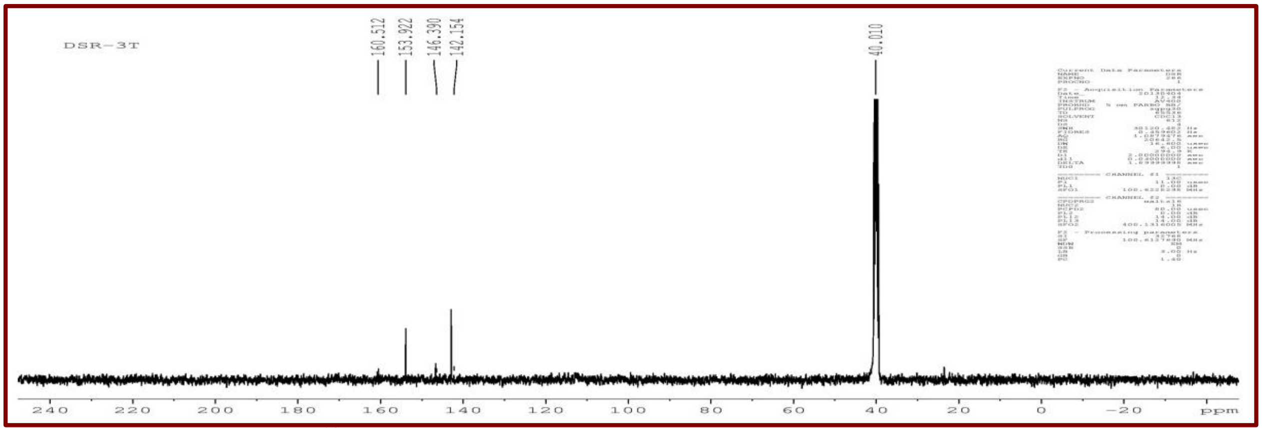


Figure 2.S9 ^{13}*C NMR spectrum of 5, 5'-(2-(1H-Tetrazol-1-yl)-1H-imidazole-4,5-diyl)bis(1H-tetrazole) (3.7)*

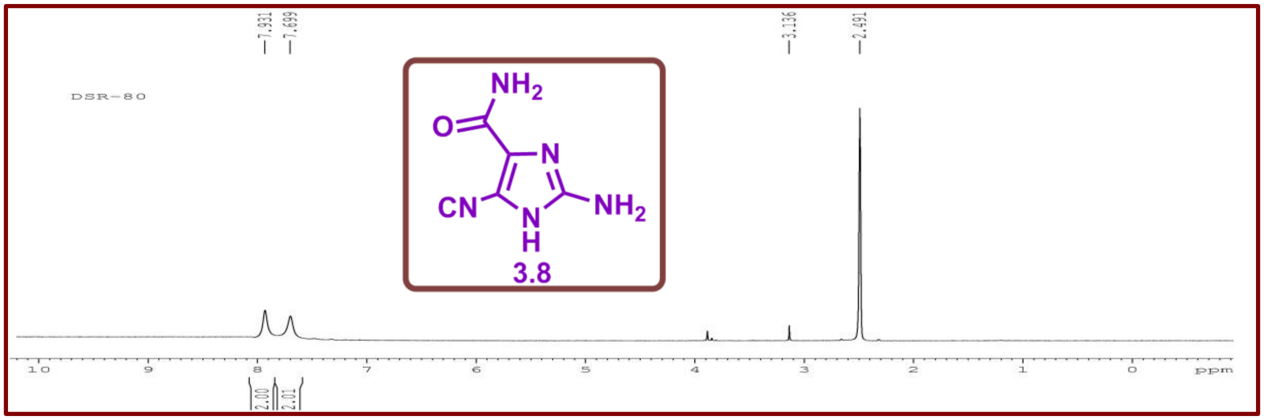


Figure 2.S10 ^{1}*H NMR spectrum of 2-Amino-5-cyano-1H-imidazole-4-carboxamide* ***(3.8)***

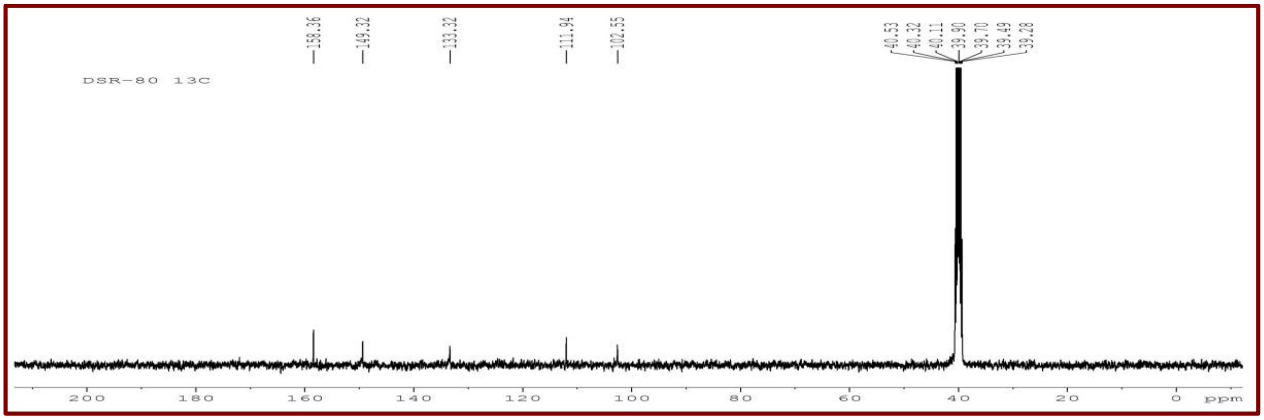


Figure 2.S11 ^{13}*C NMR spectrum of 2-Amino-5-cyano-1H-imidazole-4-carboxamide* ***(3.8)***

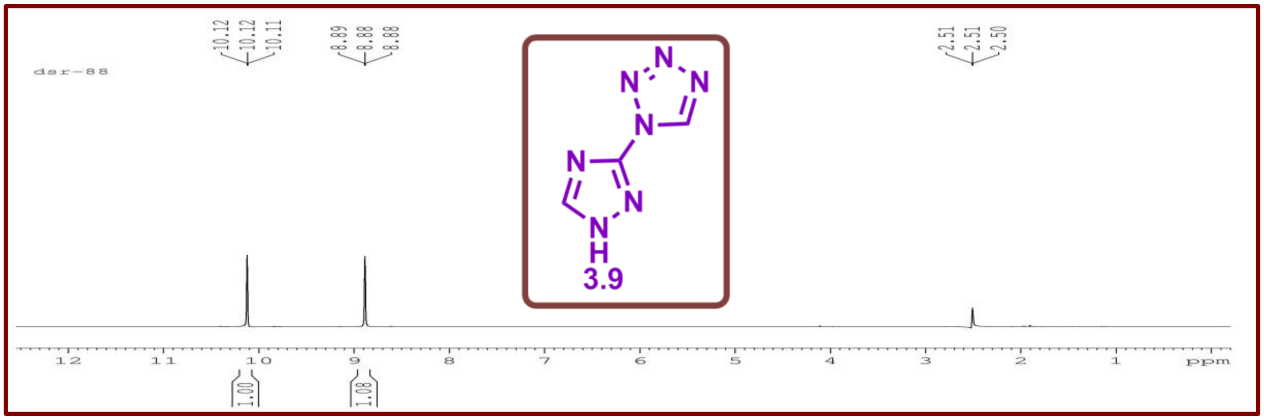


Figure 2.S12 ^{1}*H NMR spectrum of 1-(1H-1,2,4-Triazol-3-yl)-1H-tetrazole* ***(3.9)***

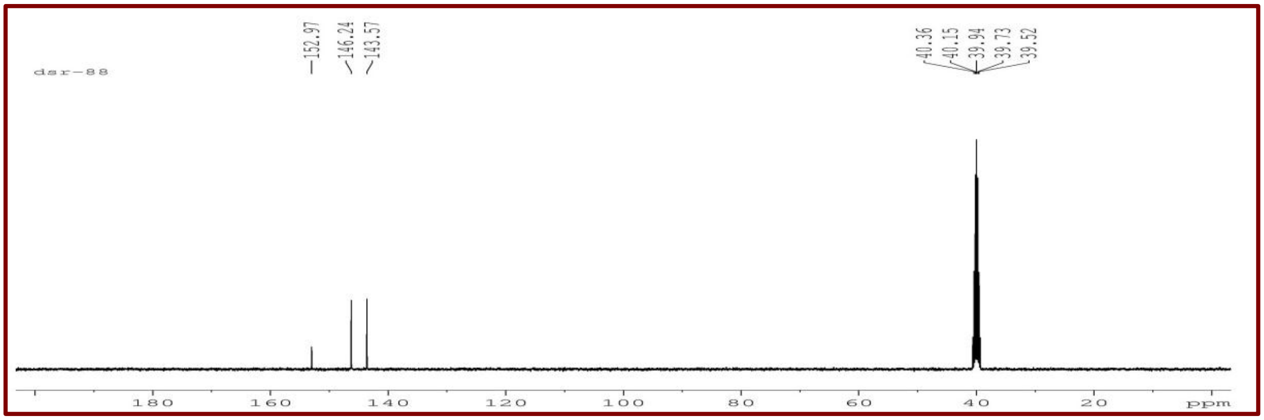


Figure 2.S13 ^{13}*C NMR spectrum of 1-(1H-1,2,4-Triazol-3-yl)-1H-tetrazole* ***(3.9)***

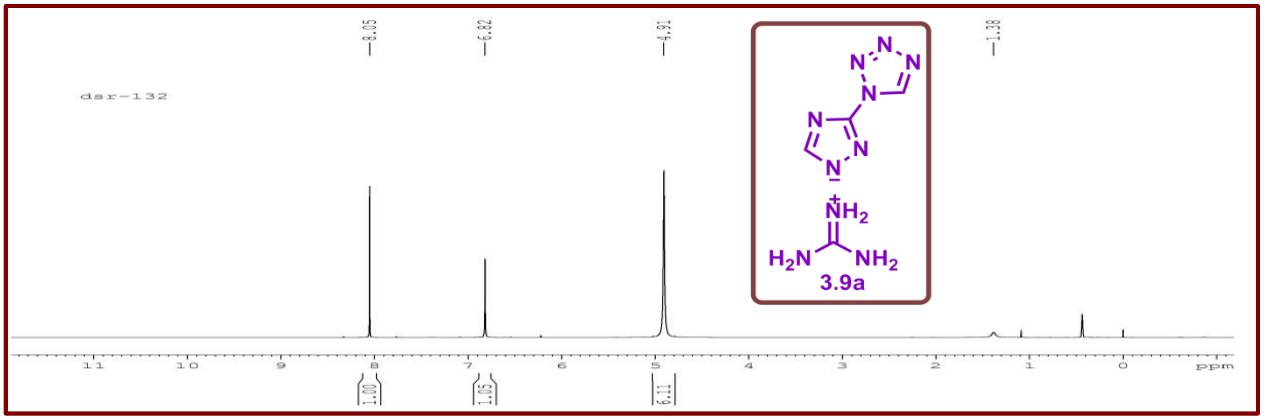


Figure 2.S14 ^{1}*H NMR spectrum of Diaminomethaniminium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9a)***

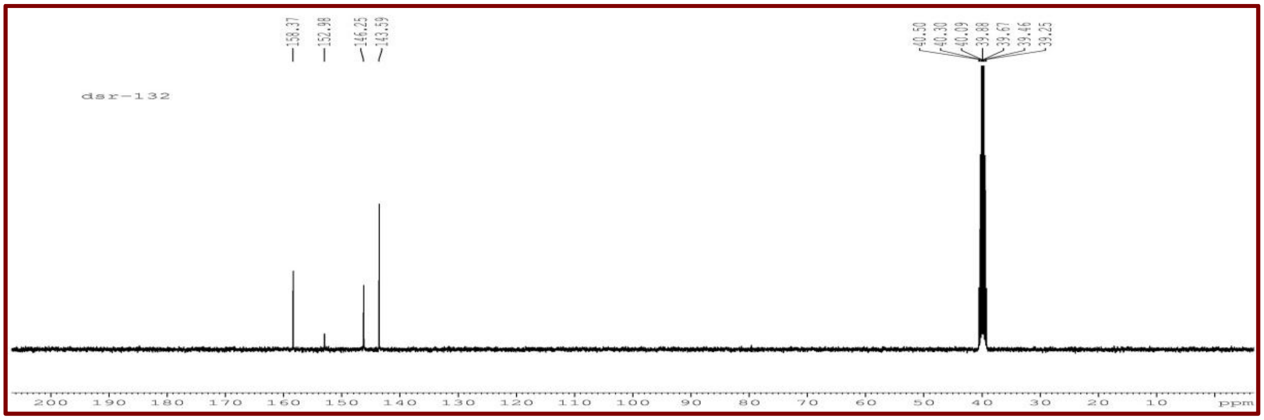


Figure 2.S15 ^{13}*C NMR spectrum of Diaminomethaniminium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9a)***

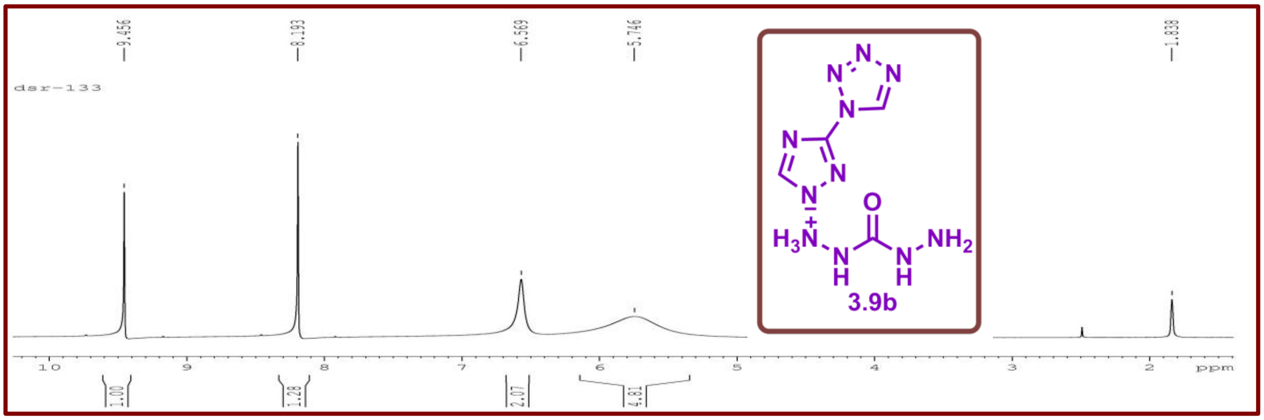


Figure 2.S16 ^{1}H NMR spectrum of (Hydrazinylcarbonyl)hydrazinium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide ***(3.9b)***

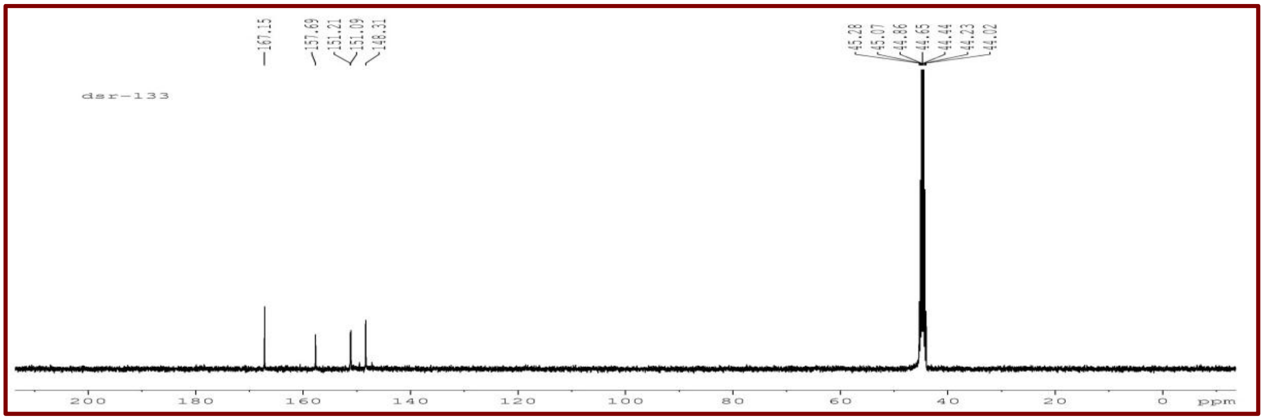


Figure 2.S17 ^{13}C NMR spectrum of (Hydrazinylcarbonyl)hydrazinium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide ***(3.9b)***

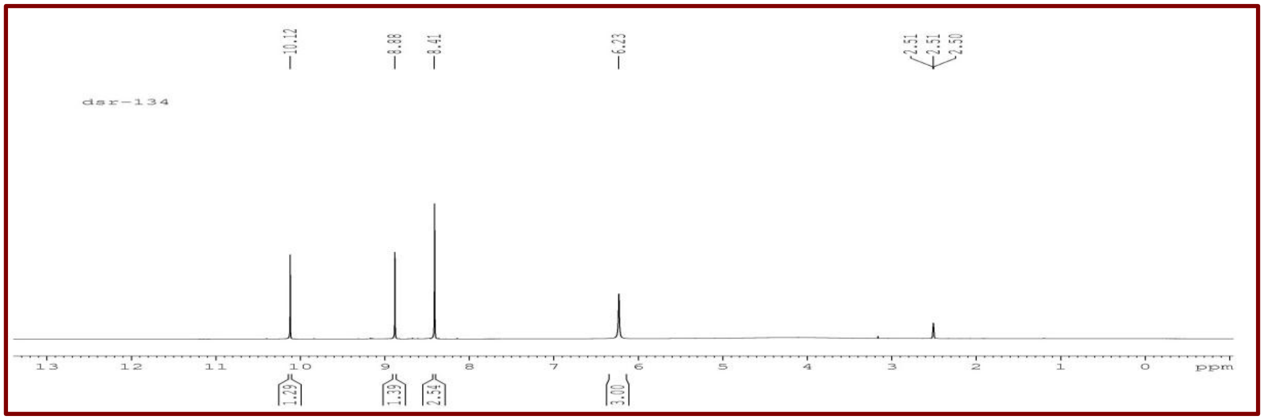


Figure 2.S18 ^{1}H NMR spectrum of 4-Amino-4H-1,2,4-triazol-1-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide ***(3.9c)***

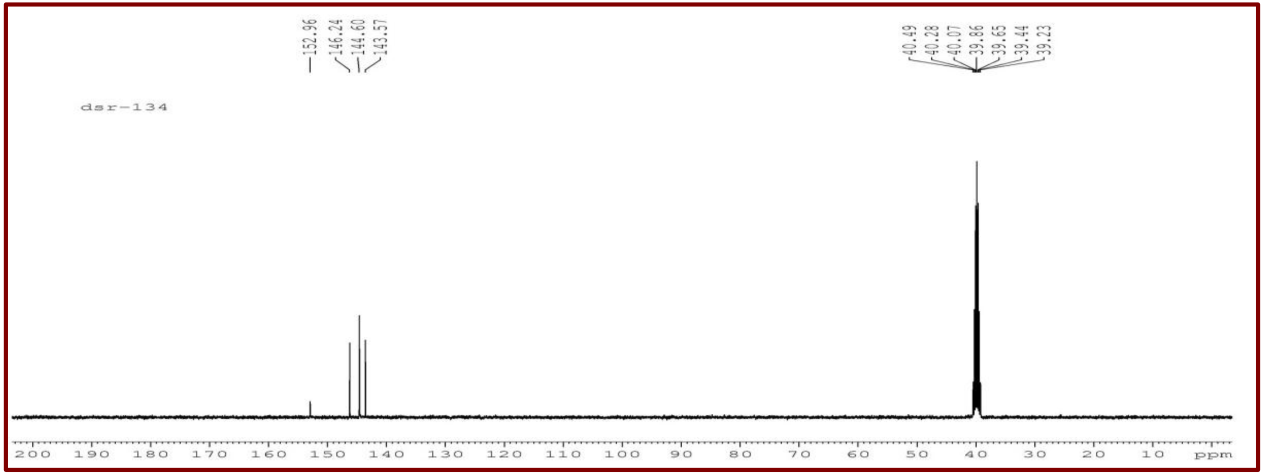


Figure 2.S19 ^{13}*C NMR spectrum of 4-Amino-4H-1,2,4-triazol-1-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9c)***

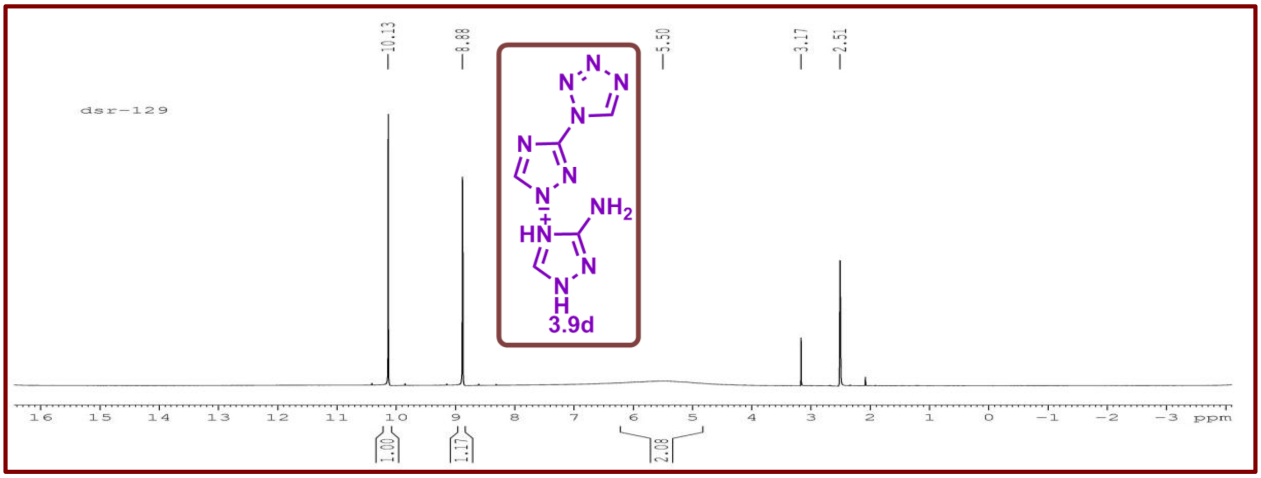


Figure 2.S20 ^{1}*H NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9d)***

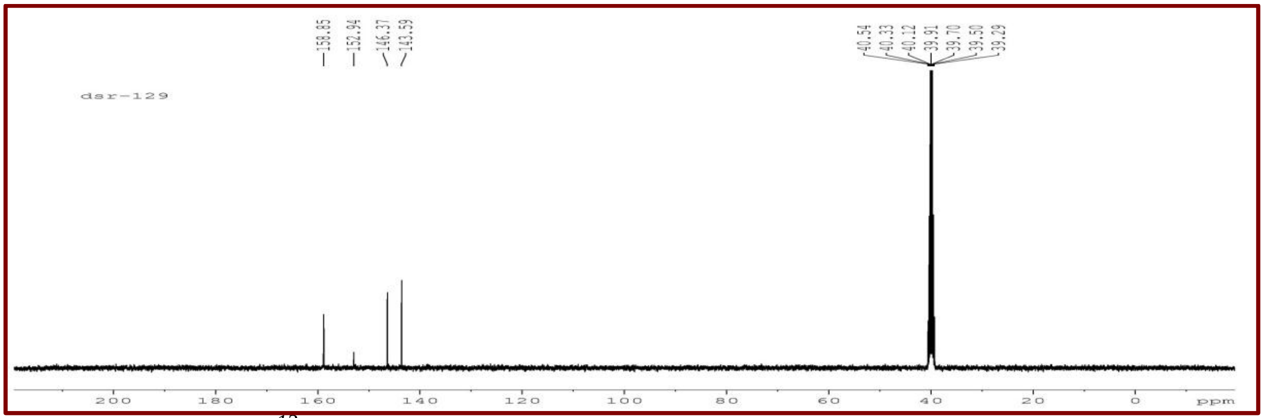


Figure 2.S21 ^{13}*C NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9d)***

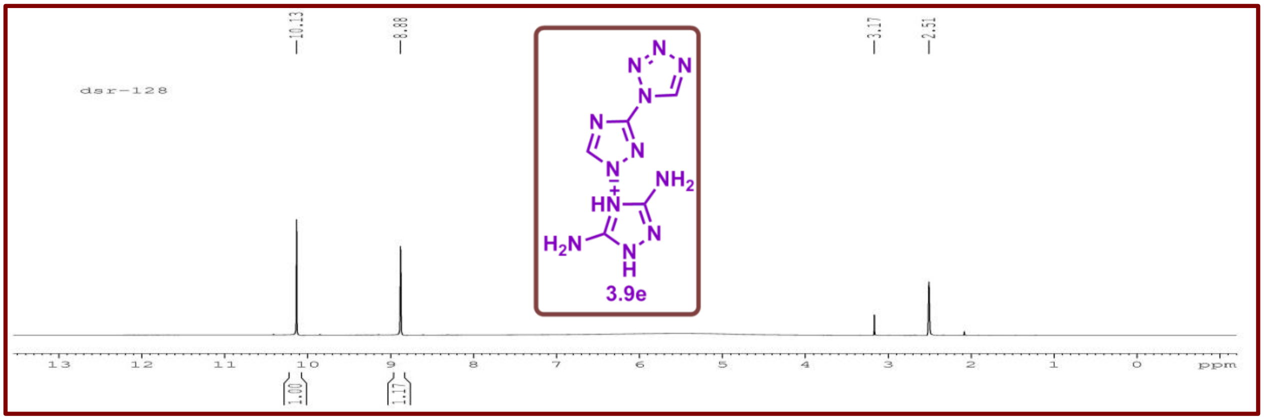


Figure 2.S22 ^{1}*H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9e)***

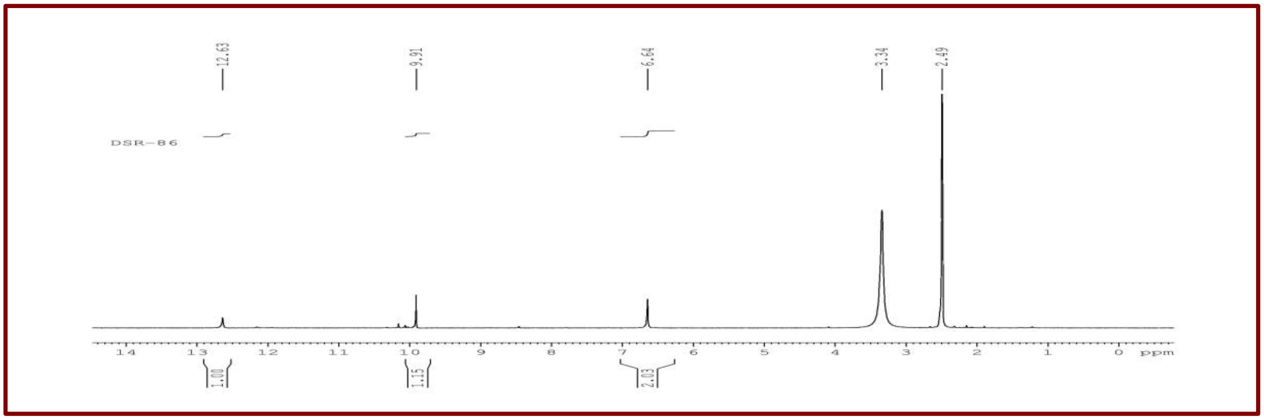


Figure 2.S23 ^{13}*C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.9e)***

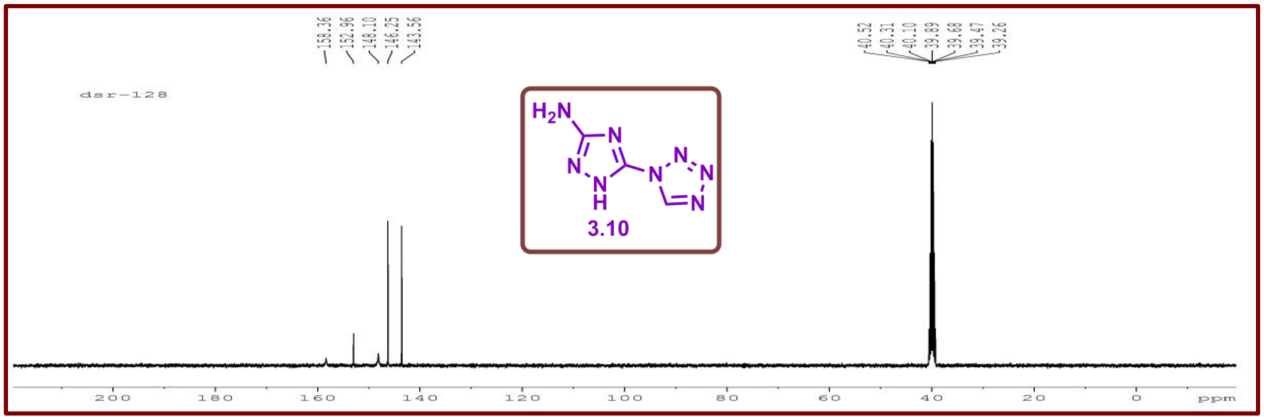


Figure 2.S24 ^{1}*H NMR spectrum of 5-(1H-Tetrazol-1-yl)-1H-1,2,4-triazol-3-amine* ***(3.10)***

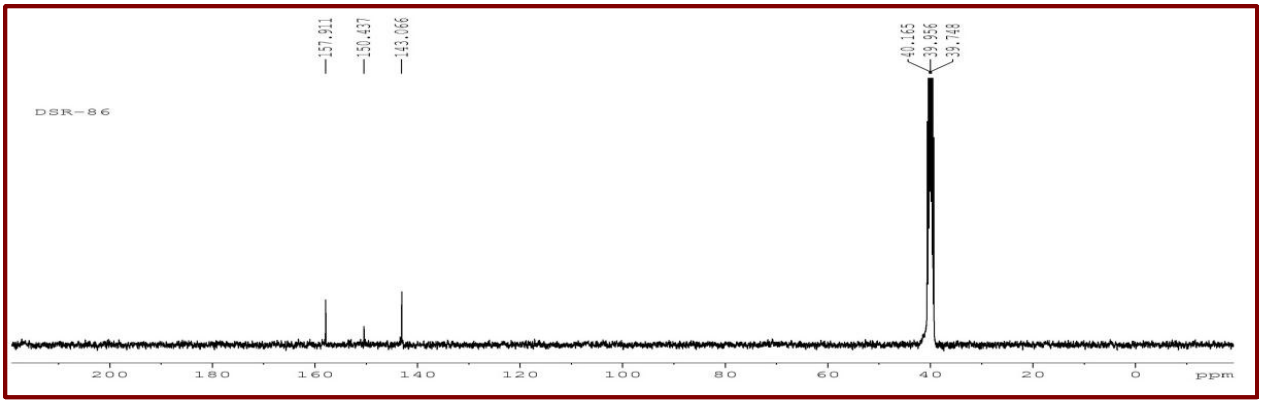


Figure 2.S25 ^{13}C NMR spectrum of 5-(1H-Tetrazol-1-yl)-1H-1,2,4-triazol-3-amine **(3.10)**

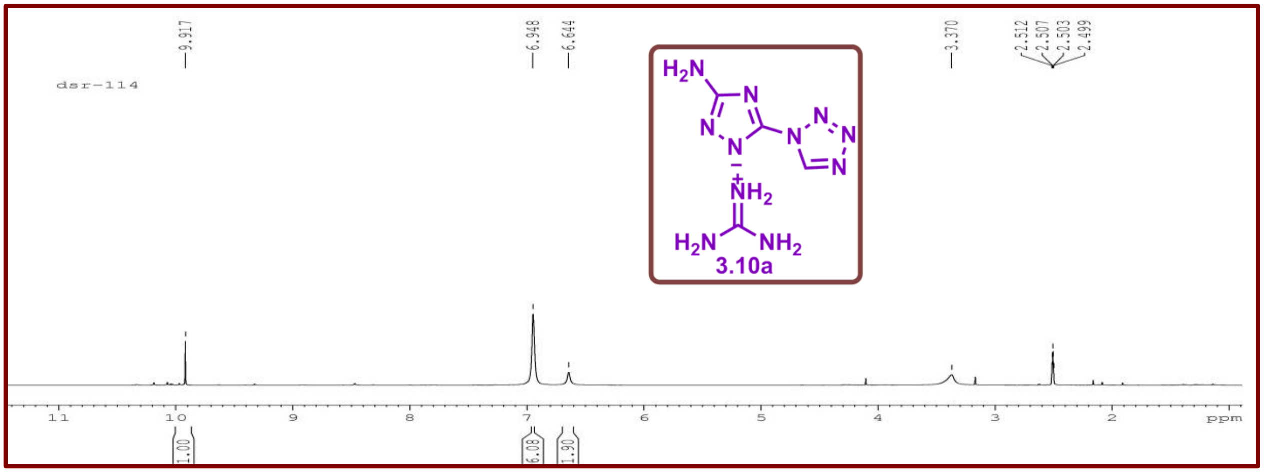


Figure 2.S26 ^{1}H NMR spectrum of Diaminomethaniminium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide **(3.10a)**

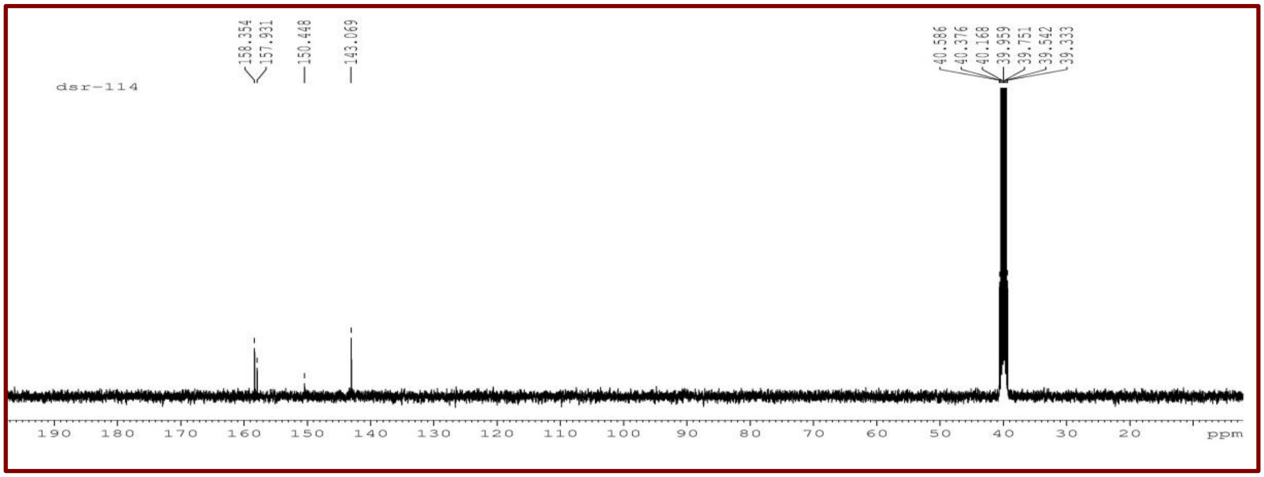


Figure 2.S27 ^{13}C NMR spectrum of Diaminomethaniminium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide **(3.10a)**

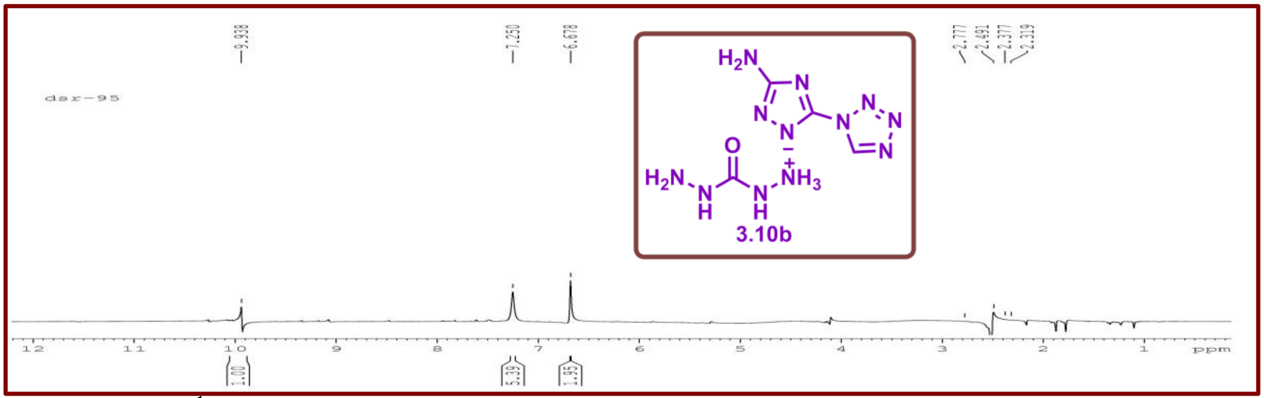


Figure 2.S28 ^{1}*H NMR spectrum of (Hydrazinylcarbonyl)hydrazonium 3-mino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.10b)***

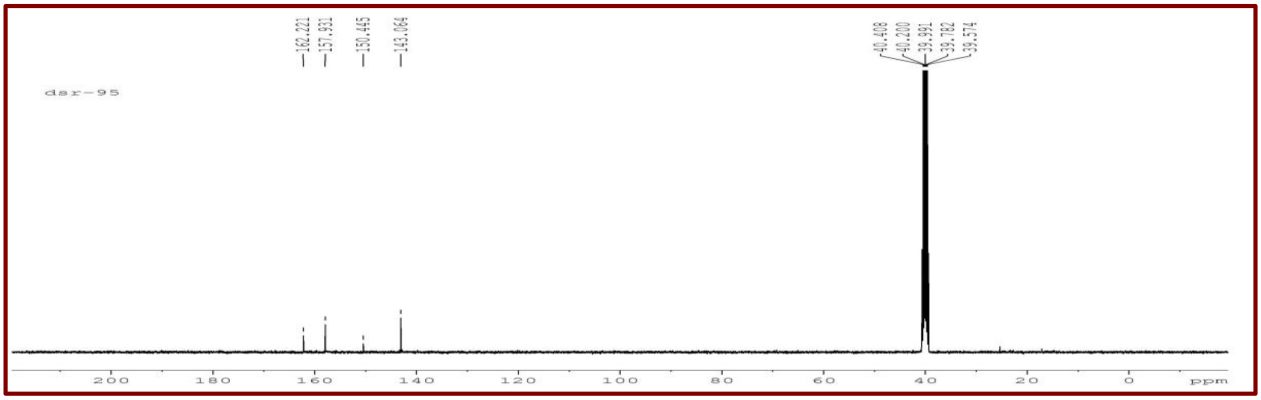


Figure 2.S29 ^{13}*C NMR spectrum of (Hydrazinylcarbonyl)hydrazonium 3-mino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.10b)***

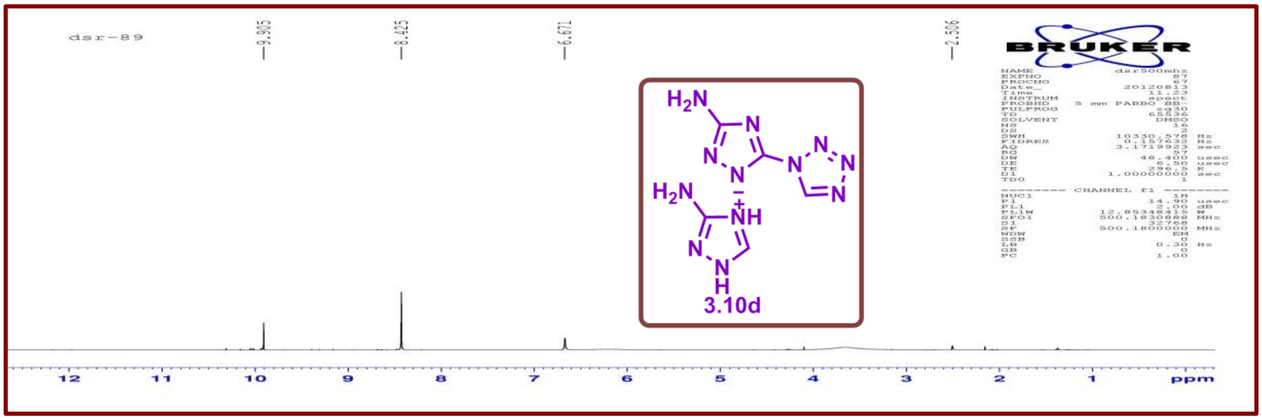


Figure 2.S30 ^{1}*H NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.10d)***

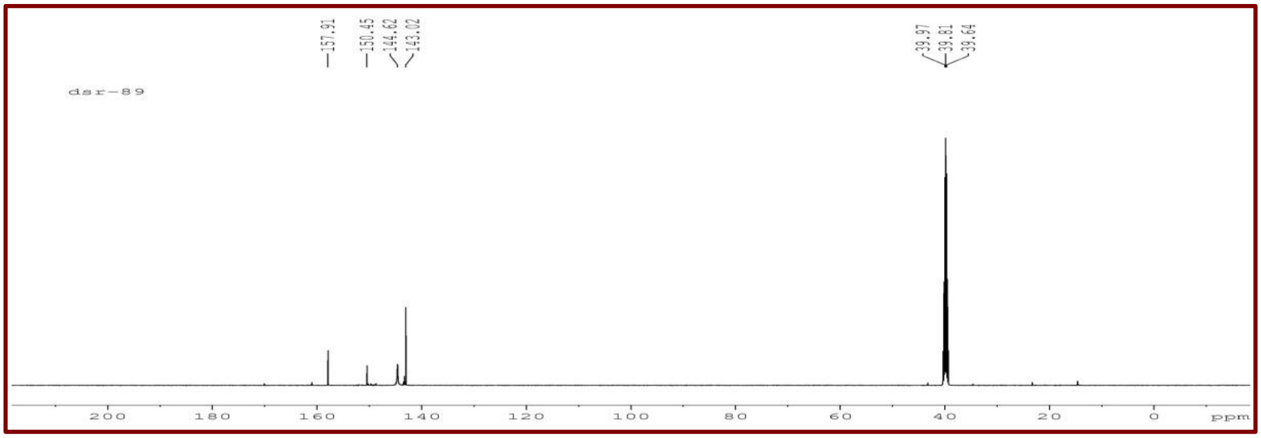


Figure 2.S31 ^{13}*C NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.10d)***

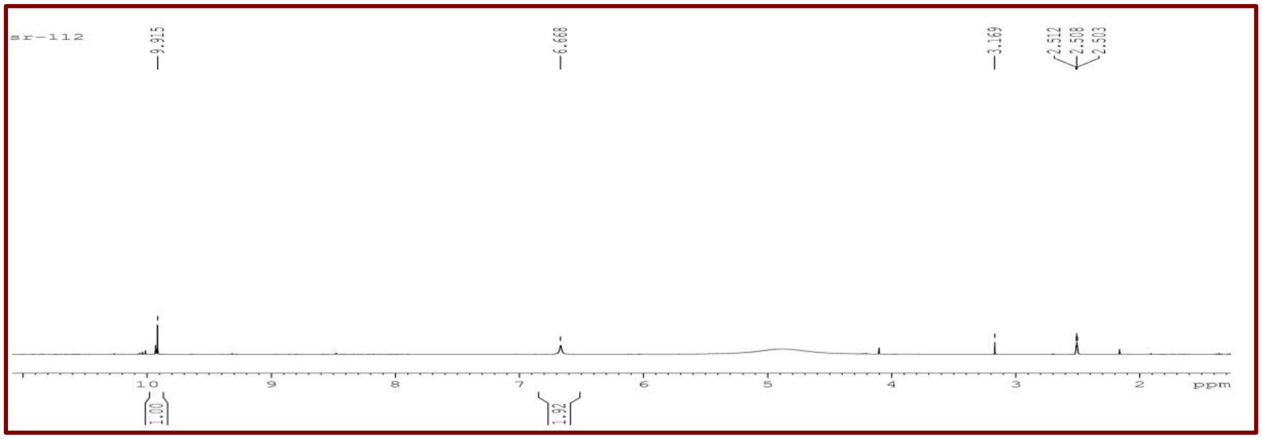


Figure 2.S32 ^{1}*H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-amino-5-(1H-tetrazol-1-yl)-1 ,2,4-triazol-1-ide* ***(3.10e)***

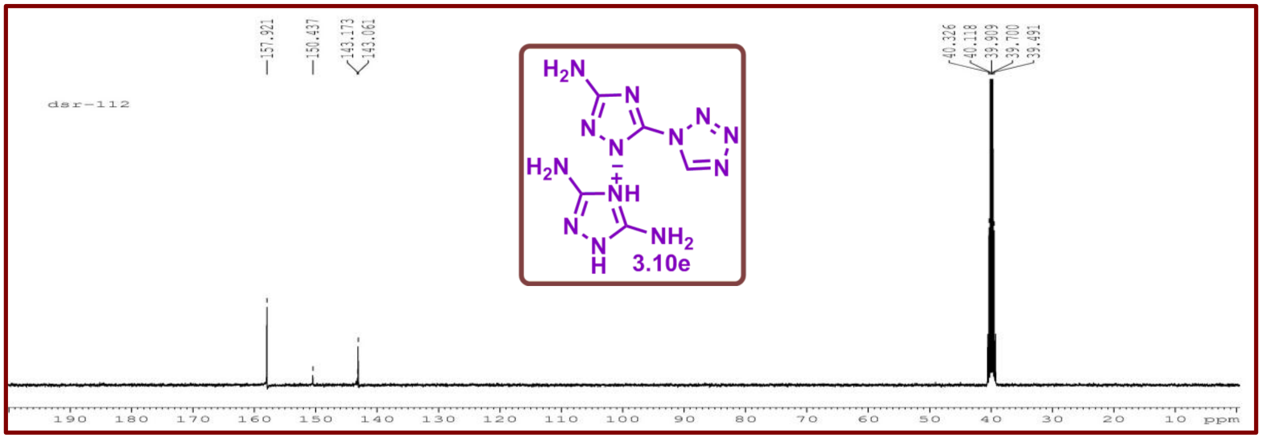


Figure 2.S33 ^{13}*C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-amino-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.10e)***

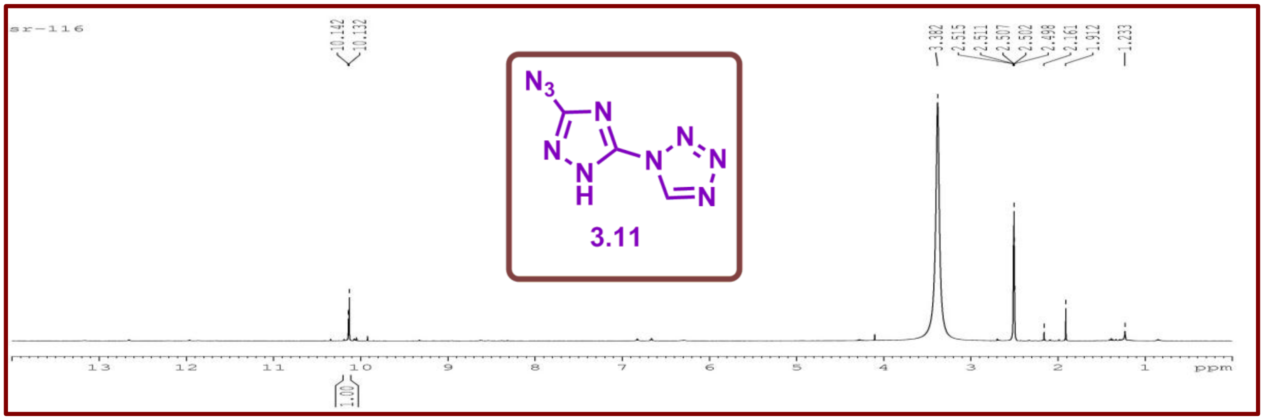


Figure 2.S34 ^{1}H NMR spectrum of 1-(3-Azido-1H-1,2,4-triazol-5-yl)-1H-tetrazole ***(3.11)***

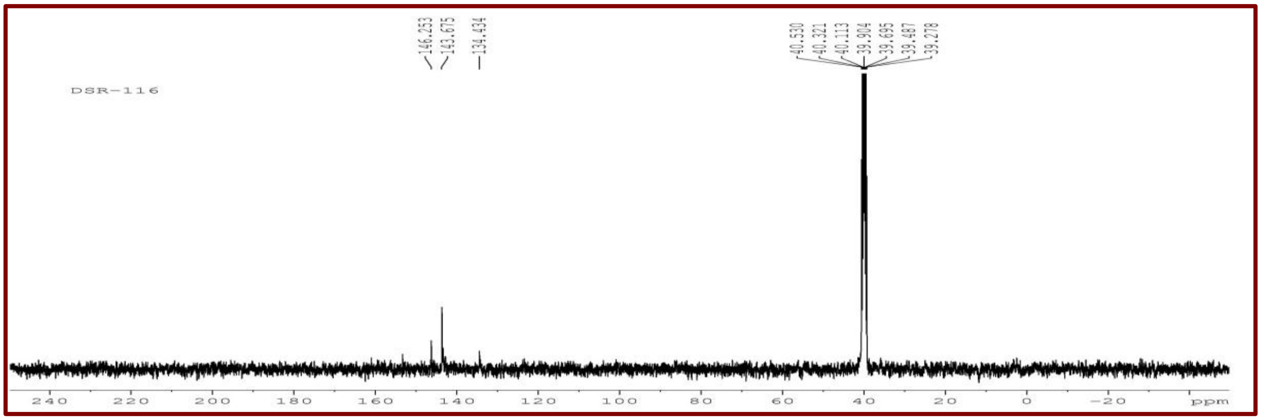


Figure 2.S35 ^{13}C NMR spectrum of 1-(3-Azido-1H-1,2,4-triazol-5-yl)-1H-tetrazole ***(3.11)***

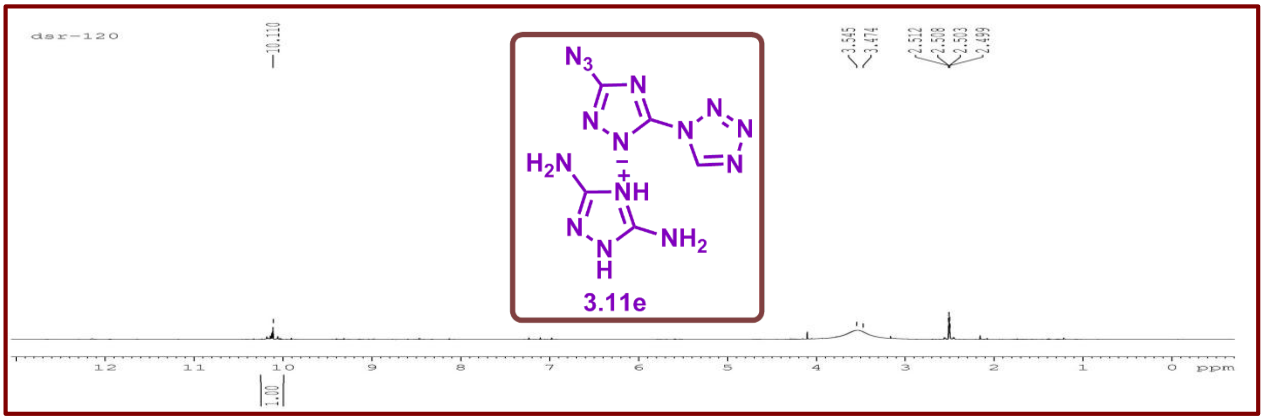


Figure 2.S36 ^{1}H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide ***(3.11e)***

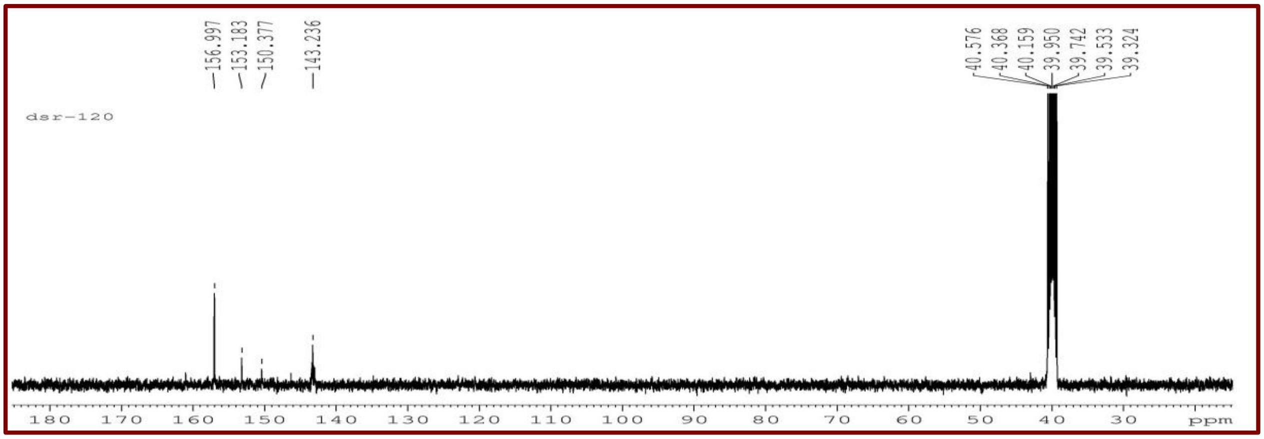


Figure 2.S37 ^{13}C *NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-5-(1H-tetrazol-1-yl)-1,2,4-triazol-1-ide* ***(3.11e)***

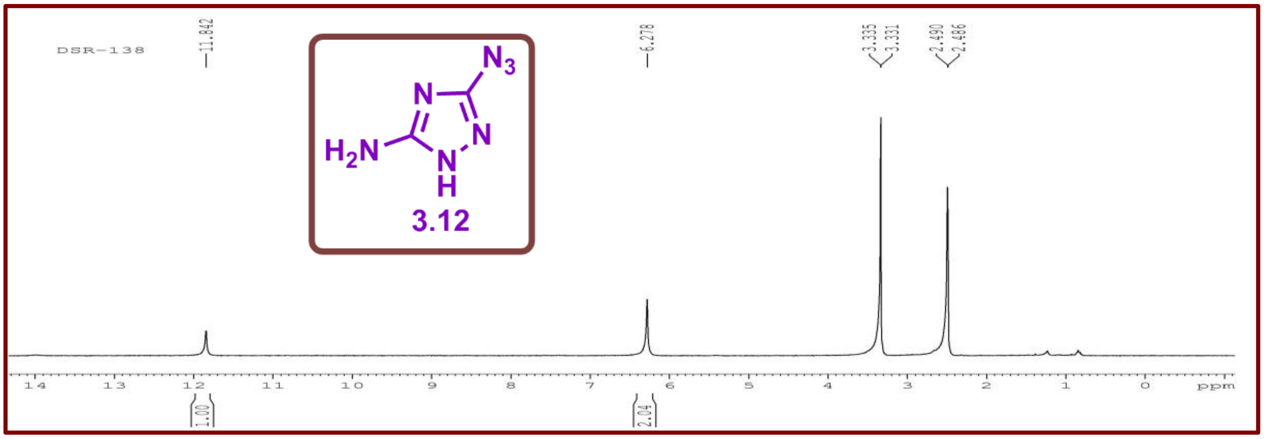


Figure 2.S38 ^{1}H *NMR spectrum of 3-Azido-1H-1,2,4-triazol-5-amine* ***(3.12)***

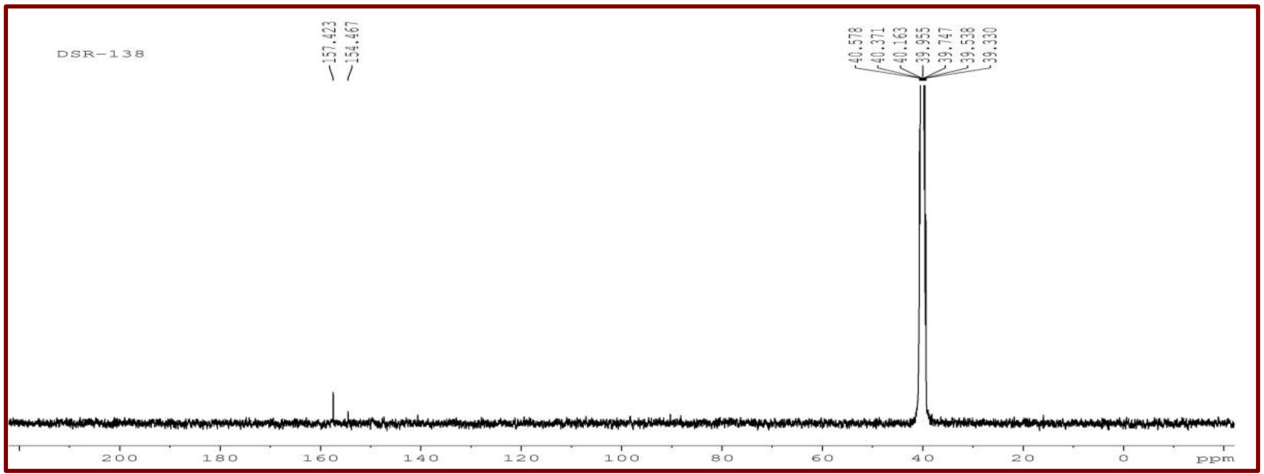


Figure 2.S39 ^{13}C *NMR spectrum of 3-Azido-1H-1,2,4-triazol-5-amine* ***(3.12)***

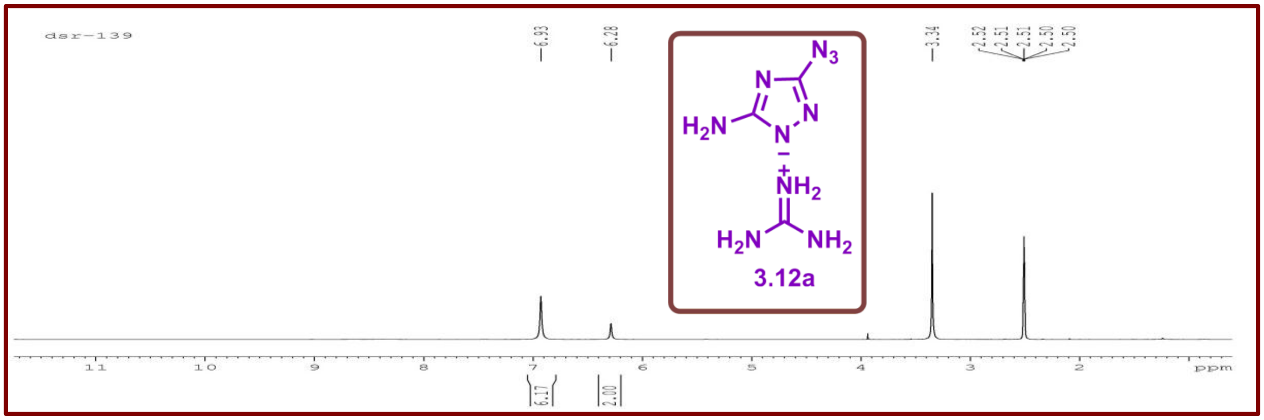


Figure 2.S40 ^1H *NMR spectrum of Diaminomethaniminium 5-amino-3-azido-1,2,4-triazol-1-ide* ***(3.12a)****.*

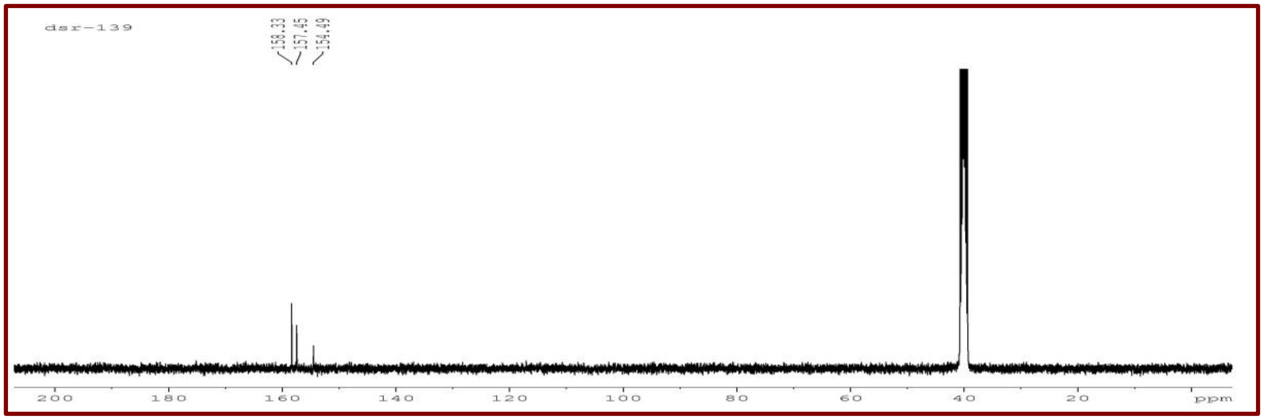


Figure 2.S41 ^{13}C *NMR spectrum of Diaminomethaniminium 5-amino-3-azido-1,2,4-triazol-1-ide* ***(3.12a)***

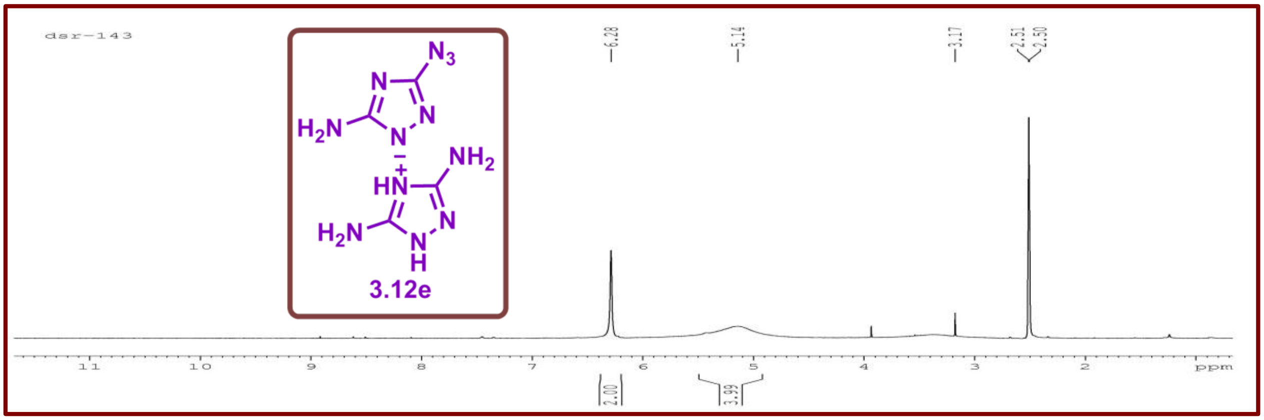


Figure 2.S42 ^1H *NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 5-amino-3-azido-1,2,4-triazol-1-ide* ***(3.12e)***

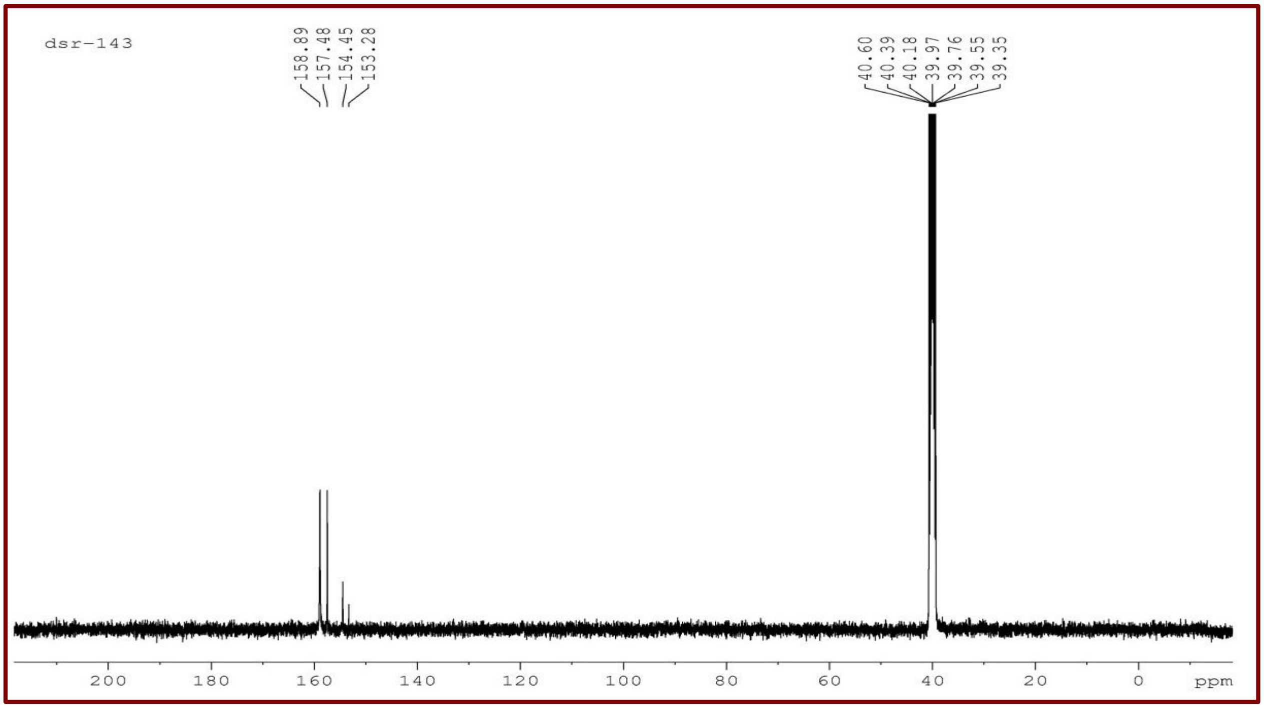


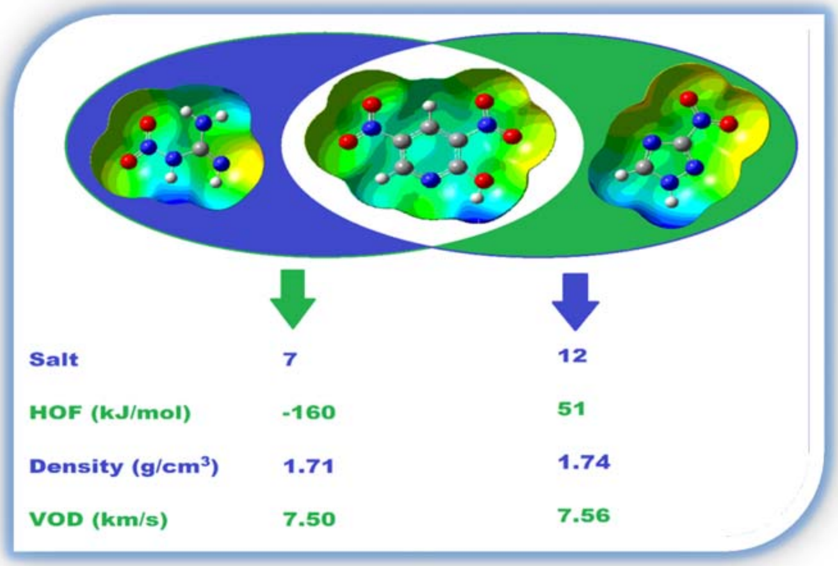
Figure 2.S43 ^{13}*C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 5-amino-3-azido-1,2,4-triazol-1-ide* ***(3.12e)***

CHAPTER 4

Energetic Monoanionic Salts of 3,5-Dinitropyridin-2-ol

Abstract

3,5-Dinitropyridin-2-ol and thirteen of its monoanionic salts (**4.1-4.13**) containing diverse cations including nitrogen-rich molecules were readily synthesized and fully characterized by ^{1}H and ^{13}C NMR, IR spectroscopy, thermogravimetric differential thermal analysis (TG-DTA), mass spectroscopy, and elemental analysis. Favourable structure–property relationships were achieved by changing the cationic moieties. The densities of the 3,5-dinitropyridin-2-ol salts range between 1.60 and 1.74 g cm^{-3}, while detonation velocities and pressures were calculated to be in the range 6.51-7.56 km s^{-1} and 17.57-24.84 GPa, respectively. Based on contributions to the energetic properties, the most promising cation for use in energetic 3,5-dinitropyridin-2-ol salts of those studied were nitroguanidine and 3-nitro-1,2,4-triazole.



Salt	7	12
HOF (kJ/mol)	-160	51
Density (g/cm^3)	1.71	1.74
VOD (km/s)	7.50	7.56

4.1. Introduction

In recent years, much attention has been given to the design and development of energetic salts containing nitrogen-rich heterocycles [1]. Due to their structural compositions, the energetic salts possess unique properties. The properties of its components can also be modified independently by changing the substituents in it. The choices of cations and anions have been nitrogen-rich heterocycles containing various explosophores. This is because these materials combine high energy content with better performance and reduced sensitivity to shock, friction and electrostatic discharge. Moreover, the compounds containing high percentage of nitrogen are environmentally friendly because their major decomposition product is expected to be N_2 gas.

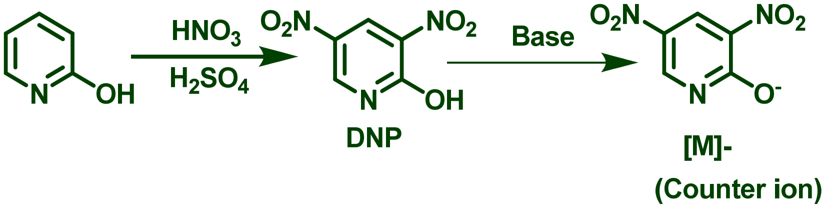
Aside from being hindered by the inherent dangers of this field, the improvement in energetic properties of novel energetic materials must achieve a challenging combination of properties including high explosive power, high stability and low production cost. Potential of the pyridine derivatives in generating the energetic materials with good performance and reasonable thermal stability has been reported [2]. However, to the best of our knowledge, the pyridine based salts are not been explored for their possible application as energetic materials. This prompted us to investigate the potential of the neutral 3, 5-dinitropyridin-2-ol compound as possible precursor for the synthesis of ionic salts.

Consequently, a report on the preparation of the energetic salts based on 3,5-dinitropyridin-2-ol anion in combination with urea, semicarbazide, carbohydrazide, biuret, guanidine, aminoguanidine, nitroguanidine, 1,3-diaminoguanidine, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 4-nitroimidazole, 3-nitro-1,2,4-triazole and 3,4-diaminofurazan as cations is given in this chapter. The cationic species considered in this study are well-known due to their energetic properties and are widely used in constructing the energetic salts. Worthy mentioning here is that the presence of NH and NO_2 groups within the same framework is expected to form strong hydrogen bonding. Considering the amount of literature on energetic materials and the recent interest in the area of energetic salts, we were keen to explore the salts of pyridine-2-ol, which remained uninvestigated.

4.2. Results and discussion

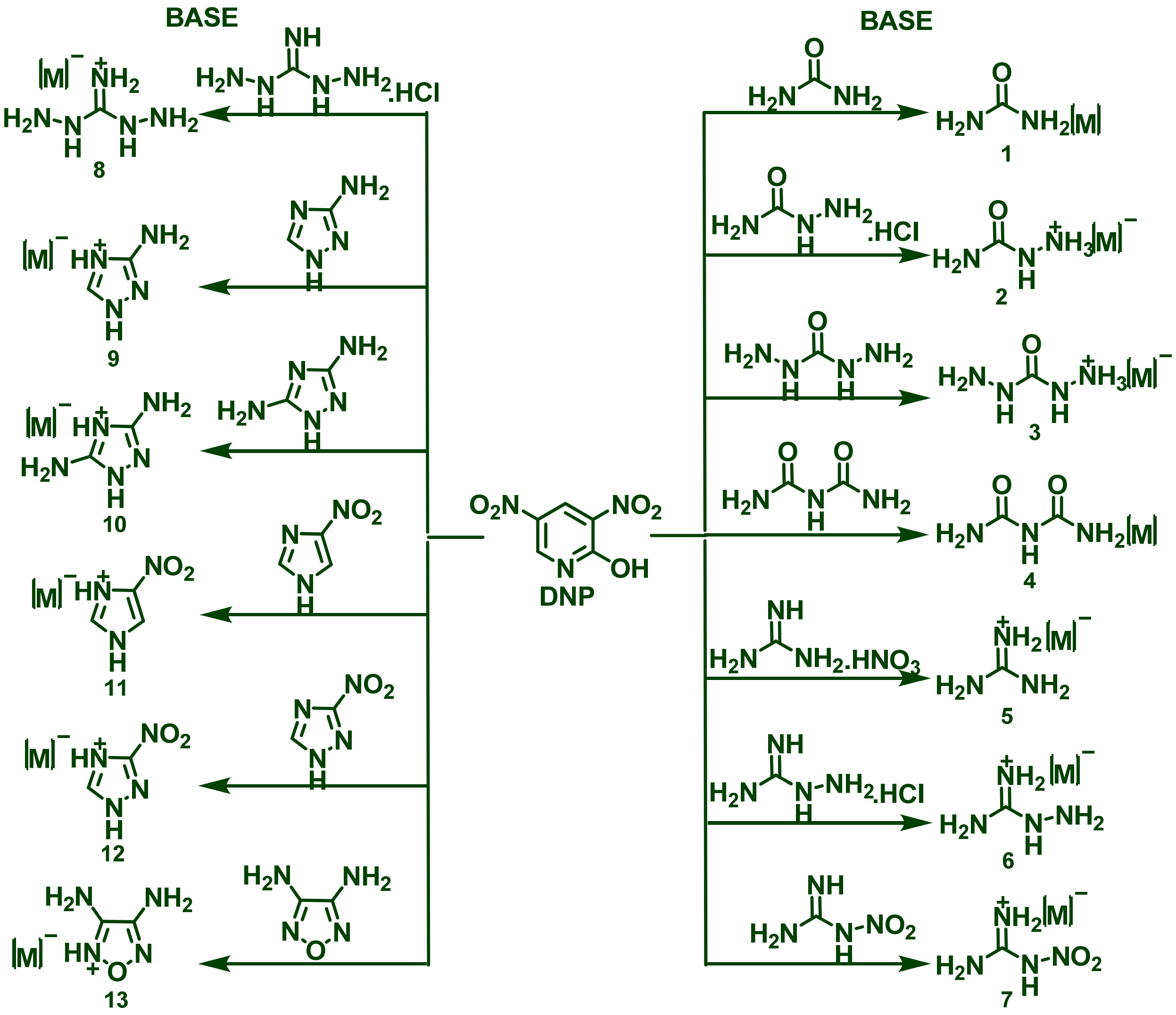
4.2.1. Synthesis and characterization

The primary requirement of an energetic compound that has high performance for practical applications is that its synthesis should be simple and achievable in the minimum number of steps. An overall synthetic protocol used for the synthesis of all the compounds described in this study is shown in Scheme 4.1 and 4.2. The nitration of 2-hydroxypyridine was performed with a mixture of concentrated sulfuric acid (98%) and nitric acid by stirring the suspension at 80 °C for 6h. After the nitration, the mixture was poured easily extracted with ethyl acetate. The synthesis of DNP was achieved by using a mixture of concentrated sulfuric acid and potassium nitrate in reasonable yield. We chose DNP mainly because of its simple synthesis and the acidity of the OH proton, which is essential for salt formation.



Scheme 4.1. Synthesis of 3,5-dinitropyridin-2-ol.

The reaction of 3,5-dinitropyridin-2-ol with an equivalent amount of semicarbazide, carbohydrazide, guanidine, aminoguanidine, nitroguanidine, 1,3-diaminoguanidine, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 4-nitroimidazole, 3-nitro-1,2,4-triazole, or 3,4-diaminofurazan, respectively, in methanol resulted in the formation of its salts **4.2, 4.3, 4.5-4.13** in excellent yields (> 90 %) and high purities (Scheme 4.2). The acidic nature of the 3,5-dinitropyridin-2-ol is high but the basicity of urea and biuret is not high enough to deprotonate 3,5-dinitropyridin-2-ol; hence, the urea adduct (**4.1**) and biuret adduct (**4.4**) are the cocrystallization product, which were obtained by the reaction of 3,5-dinitropyridin-2-ol with urea and biuret in methanol, respectively. Previously, Klapötke and co-workers [3] reported the formation of urea adduct with 2-methyl-5-nitraminotetrazolate. All this salts and adducts were isolated as powders and, except for **4.3** were non-hygroscopic and stable in air.



Scheme 4.2. *Synthesis of 3,5-dinitropyridin-2-ol salts.*

The structures of salts 1-13 were confirmed by ^{1}H, ^{13}C NMR, and IR spectroscopy as well as elemental analysis. In the ^{1}H NMR spectra, the proton signals of the anion occurred at d=8.97 and 9.06 ppm, and the other signals were assigned to the respective cations. Similarly, in the ^{13}C NMR spectra, five signals at d=154, 143, 136, 133, and 128 ppm were from the anion and the other signals were associated with the respective cations. In the IR spectra, the main absorption bands at 3230, 3046, 3010, 1654, 1572, 1528, 1341, 1298, and 1139 cm^{-1} were attributed to the O-H, C-H, C-N, C-O, C=C and C-NO_2 bonds of the anion. The intense absorption bands at 3100–3500 cm^{-1} can be assigned to the N-H bonds of the nitrogen-rich cations.

4.2.2. Thermal stabilities and energetic properties

The thermal stabilities of the DNP salts were determined by simultaneous thermogravimetric and differential scanning calorimetry analyses (DSC-TGA) conducted with a heating rate of 10 °C min^{-1}. As shown in Table 4.1, the melting points and thermal degradation temperatures of the salts were in the ranges 119– 251 °C and 169–305 °C, respectively. Whereas salt **4.3** decomposed without melting, salts **4.1**, **4.2**, and **4.4–4.13** melted with decomposition. Comparing salts **4.2** and **4.3** with **4.6** and **4.8** revealed that the guanidium salts have better thermal stabilities than the corresponding urea salts, which can delocalize the positive charge on the cations. It is expected that a delocalized positive charge over the NH group decreases the electrophilicity of the cation and results in higher thermal stability.

The heat of formation (HOF) is an important parameter that represents the energy content of the material. The HOF of the salts as well as the lattice energies were calculated by using the approach of Jenkins et al [4]. The gas phase HOF for the anions, cations, and nonionic molecules were obtained based on the isodesmic reactions.; representative reactions are shown in annexure 1. The values of the HOF for the cations and the anion are listed in Table 4.1. The heats of formation of **4.1–4.13** were calculated by using the Born–Haber cycle (Figure 4.1). The calculated values ranged from -583 to 51 kJmol^{-1}. With the exception of **4.12** (51 kJmol^{-1}), all salts have negative HOF values because of the negative HOF of the anion (377 kJmol^{-1}) and high lattice energies. The introduction of an amino group in the urea framework slightly improved the HOF values of the corresponding salts. A similar trend was evident for guanidine derivatives, **4.5, 4.6**, and **4.8**. However, the opposite effect was found in 3-amino-1,2,4-triazole (**4.9**) and 3,5-diamino- 1,2,4-triazole (**4.10**), where the presence of two amino groups on the triazole ring reduces the HOF by approximately 34 kJmol^{-1}.

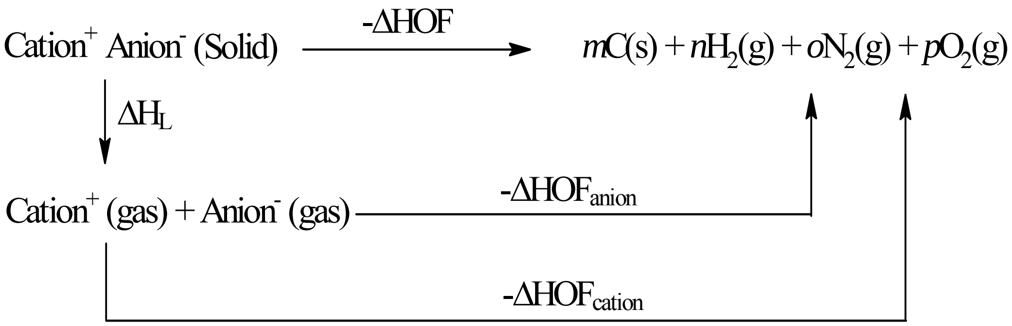


Figure 4.1. Born–Fajans–Haber cycle for the formation of energetic salts (DHL=lattice enthalpy for ionic salts; DHOFcation and DHOFanion=enthalpy of formation of the cation and anion, respectively).

The HOF and density are the most important physical properties of energetic compounds and are also involved in performance prediction. According to the Kamlet–Jacobs equations [5], detonation velocity (*VOD*) and detonation pressure (*DP*) are mainly affected by density because the detonation velocity is proportional to the density and detonation pressure is dependent on the square of the density. The densities of **4.1–4.13** were predicted by using the Hofmann approach [6], and found to range between 1.60–1.74 gcm^{-3}. Among the designed salts, **4.7** and **4.12** have the highest densities of 1.71 and 1.74 gcm^{-3}, respectively. These relatively high densities are presumably caused by the presence of additional nitro groups in the cation and the possible extensive intra and intermolecular hydrogen bonding in these salts.

Oxygen balance (OB) represents the degree to which an energetic molecule can be oxidized and is another important property for energetic materials. It is known that the performance of a material reaches its maximum value when the oxygen balance is approximately zero. As a result of zero OB, a CHNO-containing compound will be completely converted to CO_2, H_2O, and N_2. At the same time, compounds with zero OB are more prone to external stimuli. The presence of the nitro groups can improve the OB of the corresponding salts, which eventually results in higher exothermicity of the combustion and detonation process and a larger amount of gaseous byproducts [7]. The OB values of **4.1–4.13** were between -74.3– -47.1%. These salts have a higher OB than TNT (-74.0%) except for salt **4.9**. The detonation performance of the salts was calculated by Kamlet–Jacobs equations and is summarized in Table 4.1. The calculated detonation velocities (*VOD*) ranged between 6.51–7.56 kms^{-1} and the detonation pressures (*DP*) fell in the range of 17.57–24.84 GPa. Most of these salts have a higher *VOD* than TNT (*VOD*=6.88 kms^{-1}, *DP*= 19.5 GPa) [8].

The distribution of electron density is a useful parameter for understanding the reactivity and stability of molecular systems. The molecular electrostatic potential represents the charge density and polarization effects within the molecule, which are used to illustrate electrophilicity and nucleophilicity in the molecule. The surface is taken to be the 0.001 au (electrons/Bohr^3) contour of the electronic density, as proposed by Bader et al [9]. In DNP, a large electronegative potential is located in the vicinity of the NO_2 groups, the oxygen atom, and a small electronegative region near the ring nitrogen atom. The electropositive potential generated over the hydrogen atom of the hydroxy group because of the strong electron withdrawing effect of the nitro groups and pyridine ring shows the acidity of this proton and the chances that salts will be formed. In the cations that contain C=O groups (**4.1-4.4**), the charge density is mostly located on the oxygen atom because of its strong electron-withdrawing effect. Similarly, in guanidine derivatives **4.5–4.8**, charge densities were found on the nitrogen atom of the C=N bond. In salts **4.9, 4.10**, and **4.13**, the electron densities gathered on the ring nitrogen atoms, rather than the substituted NH_2 groups.

*Table 4.1. Energetic properties of 3,5-dinitropyridin-2-ol (**DNP**) and its salts (**4.1-4.13**).*

Compd	OB[a]	HOF$_c$[b]	HOF$_a$[c]	U_{Pot}[d]	H$_L$[e]	HOF$_{salt}$[f]	ρ[g]	VOD[h]	DP[i]	Q[j]	T$_{dec}$[k]	Mp[l]
DNP	-56.2	--	--	--	--	-201[m]	1.73	7.12	21.96	1098	287	171
4.1	-62.0	491	-3770	498	503	-389	1.65	6.80	19.47	926	233	138
4.2	-61.5	531	-3770	488	493	-339	1.64	6.87	19.80	939	196	162
4.3	-61.1	620	-3770	479	484	-242	1.63	7.01	20.53	992	169	--
4.4	-61.1	274	-3770	475	480	-583	1.66	6.60	18.35	809	206	185
4.5	-72.1	567	-3770	495	499	-310	1.61	6.51	17.57	837	205	145
4.6	-71.0	658	-3770	486	491	-210	1.61	6.69	18.47	901	233	119
4.7	-47.1	701	-3770	479	484	-160	1.71	7.50	24.19	1137	268	162
4.8	-70.1	776	-3770	477	482	-83	1.60	6.88	19.50	982	216	126
4.9	-74.3	796	-3770	484	489	-69	1.65	6.69	18.79	953	230	212
4.10	-73.2	754	-3770	475	480	-103	1.64	6.63	18.42	893	256	251
4.11	-64.4	770	-3770	473	478	-85	1.69	7.10	21.55	1144	305	161
4.12	-50.8	910	-3770	477	482	51	1.74	7.56	24.84	1231	236	140
4.13	-64.6	850	-3770	478	483	-10	1.67	7.13	21.52	1114	267	122

[a]Oxygen balance (%). [b]Heat of formation of cation (kJmol^{-1}). [c]Heat of formation of anion (kJmol^{-1}). [d]Lattice potential energy (kJmol^{-1}). [e]Lattice energy (kJmol^{-1}). [f]Heat of formation of salt (kJmol^{-1}). [g]Density (gcm^{-3}). [h]Velocity of detonation (kms^{-1}). [i]Detonation pressure (GPa). [j]Chemical energy of detonation (calg^{-1}). [k]Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10 C min^{-1}). [l]Melting point (°C). [m]Solid state heat of formation calculated by subtracting heat of sublimation (82.40 kJmol^{-1}) from its gas phase heat of formation (-118.38 kJmol^{-1}) [10].

4.3. Summary

Energetic DNP-based salts were successfully synthesized and fully characterized. The salts have good physical and detonation properties, including good thermal stability. In particular, salts **4.7** (ρ =1.71 gcm^{-3}, *VOD*=7.50 kms^{-1} and *DP*= 24.19 GPa) and **4.12** (ρ =1.74 gcm^{-3}, *VOD*=7.56 kms^{-1} and *DP*= 24.84 GPa) have excellent thermal stability (Tdec>236 °C) and high density, which gives remarkable enhancement of the detonation velocity and pressure when compared to other salts. Our results showed moderate performances, which were expected to improve for oxygen-balanced mixtures with a suitable oxidizer. We have demonstrated the ability of this class of DNP salts to act as energetic materials. The mixture of these salts with an oxidizer to improve the oxygen balance and performance will be the focus of future work in our group.

4.4. Experimental section

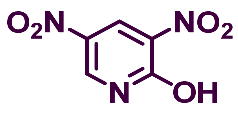
4.4.1. Materials and instrumentation

The reagents were available commercially and were used as purchased without further purification. Reactions were monitored by TLC analysis on precoated silica gel TLC plates obtained from Merck. ^{1}H and ^{13}C NMR spectroscopic data were recorded on a Bruker Avance 400 MHz FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard and [D6]DMSO as the solvent. Mass analysis was performed on a LC-MS spectrometer. Melting points and decomposition temperatures were determined by DSC-TGA on a TA Instruments SDT Q600 instrument. The IR spectra were recorded on a Perkin–Elmer IR spectrometer by using KBr pellets. The HRMS were recorded on a Bruker Maxis instrument. Elemental analyses were performed on a flash EA 1112 full automatic trace element analyzer.

4.4.2. Synthetic Procedures

***3,5-Dinitropyridin-2-ol (DNP)*:** The preparation of DNP is given in Scheme 4.1. In this work, DNP was prepared using two different pathways, (I) pyridin-2-ol (0.285 mg, 3 mmol) was added slowly to a solution of fuming nitric acid (7 mL) and conc. sulfuric acid (12 mL) stirred at 0 °C. The reaction mixture was kept stirring for 1 h at 0 °C and subsequently for 6 h at 80 °C. The contents were cooled, poured into crushed ice and neutralized with sodium carbonate. The neutralized solution was extracted with ethyl acetate. The organic phase was dried with Na_2SO_4 and evaporated to give a light yellow product in 45% yield. (II) A round-bottom flask was charged with sulfuric acid (98%, 15mL) and cooled to approximately 5 °C. Potassium nitrate (1.011 g, 10 mmol) was added slowly with stirring to avoid rise in the temperature. After complete addition of potassium nitrate, reaction mixture stirred for 15 min and pyridin-2-ol (0.285 mg, 3 mmol) was added at a rate such that the temperature did not exceed 10 °C.

Vigorous stirring was maintained to prevent concentrating the solid in the center. After complete pyridin-2-ol addition, the cooling bath was removed and the reaction was stirred for an additional 1 hr at 60 °C. The reaction mixture poured into crushed ice and resulting precipitate was isolated by filtration, washed with cold 10% HCl and water. The resultant yellow solid was air dried to afford desired product (49%). DSC-TGA (Heating rate: 10 °C min^{-1}): 287 °C (dec.).



DNP

IR (KBr pellet, ν_{max}/cm^{-1}) : 3233, 3046, 3013, 1693, 1654, 1626, 1572, 1528, 1424, 1363, 1341, 1298, 1139, 744, 700.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.05 (s, 1H), 8.07 (s, 1H) ppm (s, 2H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 154.6, 143.8, 136.6, 133.4, 128.4.

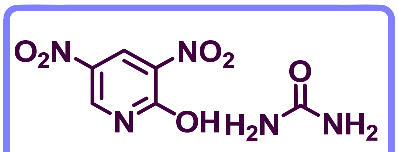
Mass : 186.

Anal. Calcd. for $C_5H_3N_3O_5$: C, 32.44; H, 1.63; N, 22.70.

Found : C, 32.38; H, 1.70; N, 22.60.

General procedure for the synthesis of the salts 4.1-4.13: A solution of 3,5-dinitropyridin-2-ol (185 mg, 1 mmol) in 6 mL methanol was added to a solution of urea (0.060 mg, 1 mmol), semicarbazide hydrochloride (0.112 mg, 1 mmol), carbohydrazide (0.090 mg, 1 mmol), biuret (0.103 mg, 1 mmol), guanidine nitrate (0.122 mg, 1 mmol), aminoguanidine hydrochloride (0.111 mg, 1 mmol), nitroguanidine (0.104 mg, 1 mmol), 1,3-diaminoguanidine monohydrochloride (0.126 mg, 1 mmol), 3-amino-1,2,4-triazole (0.084 mg, 1 mmol), 3,5-diamino-1,2,4-triazole (0.099 mg, 1 mmol), 4-nitroimidazole (0.113 mg, 1 mmol), 3-nitro-1,2,4-triazole (0.114 mg, 1 mmol), or 3,4-diaminofurazan (0.100 mg, 1 mmol) in 7 mL methanol, respectively. The reaction was stirred for 5h at 25 °C. The solvent was evaporated under reduced pressure and the product was washed with diethyl ether and dried.

Urea-3,5-dinitropyridin-2-ol (4.1): Pale yellow product (94 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 233 °C (dec.1), 299 °C (dec.2).



4.1

IR (KBr pellet, ν_{max}/cm^{-1}) : 3495, 3407, 3205, 3095, 1703, 1681, 1626, 1582, 1511, 1347, 1314, 1248, 1128, 1188.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.01 (s, 1H), 8.94 (s, 1H), 4.71 (s, 5H).

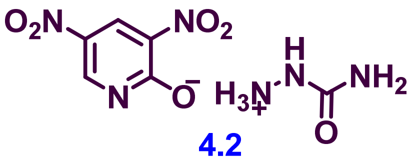
^{13}C NMR (100MHz, DMSO) : δ (ppm) 160.6, 154.8, 143.9, 136.3, 133.4, 128.4.

Mass : 246.

Anal. Calcd. for $C_6H_7N_5O_6$: C, 29.40; H, 2.88; N, 28.57.

Found : C, 29.31; H, 2.90; N, 28.48.

Carbamoylhydrazinium 3,5-dinitropyridin-2-olate (4.2): Yellow product (93 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 196 °C (dec.1), 249 °C (dec.2).



4.2

IR (KBr pellet, ν_{max}/cm^{-1}) : 3424, 3314, 3249, 3079, 2870, 2662, 1681, 1626, 1478, 1347, 1309, 1237, 1177, 1134, 876.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.99 (s, 1H), 8.95 (s, 1H), 8.85 (s, 1H), 6.55 (s, \ 2H).

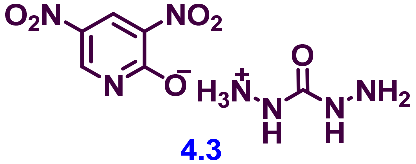
^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.2, 154.5, 143.7, 136.6, 133.3, 128.4.

Mass : 261.

Anal. Calcd. for $C_6H_8N_6O_6$: C, 27.70; H, 3.10; N, 32.30.

Found : C, 27.64; H, 2.99; N, 32.41.

***(Hydrazinylcarbonyl)hydrazinium 3,5-dinitropyridin-2-olate* (4.3):** Red product (93 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 157 °C (dec.1), 265 °C (dec.2).



4.3

IR (KBr pellet, ν_{max}/cm^{-1}) : 3315, 1692, 1621, 1517, 1429, 1352, 1303, 1155.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.97 (s, 1H), 8.69 (s, 1H).

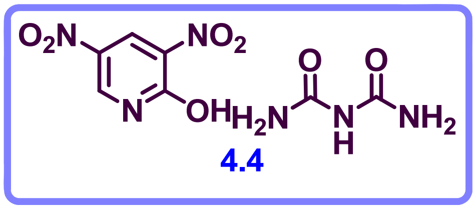
^{13}C NMR (100MHz, DMSO) : δ (ppm) 160.0, 149.5, 134.7, 133.0, 131.0, 127.4.

Mass : 276.

Anal. Calcd. for $C_6H_9N_7O_6$: C, 26.19; H, 3.30; N, 35.63.

Found : C, 26.27; H, 3.12; N, 35.58.

***Dicarbonimidic diamide-3,5-dinitropyridin-2-ol* (4.4):** Pale yellow product (94 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 216 °C (dec.1), 267 °C (dec.2).



4.4

IR (KBr pellet, ν_{max}/cm^{-1}) : 3490, 3462, 3364, 3188, 3007, 1714, 1698, 1615, 1572, 1396, 1308, 1204, 1182, 1139.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.04 (s, 1H), 8.98 (s, 1H), 8.51 (s, 1H), 6.78 (s, 5H).

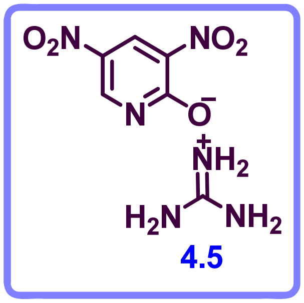
^{13}C NMR (100MHz, DMSO) : δ (ppm) 155.8, 154.6, 143.8, 136.5, 133.4, 128.4.

Mass : 289.

Anal. Calcd. for $C_7H_8N_6O_7$: C, 29.18; H, 2.80; N, 29.16.

Found : C, 29.24; H, 2.70; N, 29.24.

***Diaminomethaniminium 3,5-dinitropyridin-2-olate* (4.5)**: White product (92 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 205 °C (dec.).



4.5

IR (KBr pellet, ν_{max}/cm^{-1}) : 3380, 3194, 3079, 1676, 1572, 1615, 1533, 1352, 1314, 1215, 1182, 1128, 941.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.05 (s, 1H), 8.97 (s, 1H), 6.97 (s, 6H).

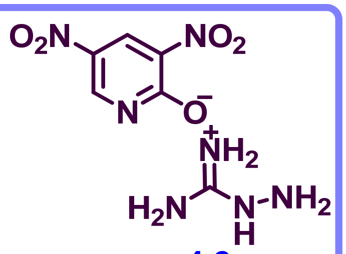
^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.3, 154.6, 143.9, 136.5, 133.4, 128.4.

Mass : 245.

Anal. Calcd. for $C_6H_8N_6O_5$: C, 29.51; H, 3.30; N, 34.42.

Found : C, 29.56; H, 3.21; N, 34.57.

***Amino(hydrazinyl)methaniminium 3,5-dinitropyridin-2-olate* (4.6):** Yellow product (95 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 232 °C (dec.).



4.6

IR (KBr pellet, ν_{max}/cm^{-1}) : 3380, 3287, 3166, 3079, 1621, 1577, 1522, 1347, 1308, 1237, 1133.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.00 (s, 1H), 8.96 (s, 1H).

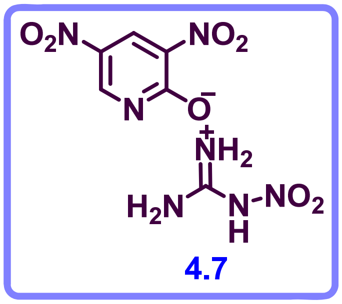
^{13}C NMR (100MHz, DMSO) : δ (ppm) 159.6, 154.5, 143.8, 136.6, 133.3, 128.4.

Mass : 260.

Anal. Calcd. for $C_6H_9N_7O_5$: C, 27.80; H, 3.50; N, 37.83.

Found : C, 27.71; H, 3.44; N, 37.90.

Amino(nitroamino)methaniminium 3,5-dinitropyridin-2-olate ***(4.7)*:** Yellow product (96 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 199 °C (dec.1), 268 °C (dec.2).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3446, 3391, 3205, 3013, 1688, 1655, 1616, 1567, 1528, 1419, 1304, 1227, 1134, 1052, 811.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.95 (s, 1H), 8.87 (s, 1H), 7.32 (s, 5H).

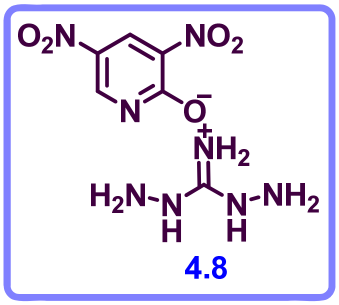
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.3, 154.6, 143.8, 136.6, 133.4, 128.4.

Mass : 290.

Anal. Calcd. for $C_6H_7N_7O_7$: C, 24.92; H, 2.44; N, 33.91.

Found : C, 24.84; H, 2.32; N, 33.88.

Dihydrazinylmethaniminium 3,5-dinitropyridin-2-olate ***(4.8)*:** Brown product (97 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 216 °C (dec.).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3452, 3315, 3243, 3084, 1687, 1627, 1572, 1523, 1424, 1358, 1309, 1227, 1139, 997.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.01 (s, 1H), 8.97 (s, 1H).

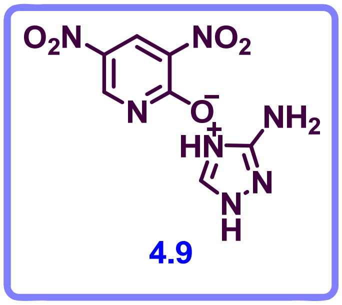
^{13}C NMR (100MHz, DMSO) : δ (ppm) 160.4, 154.6, 143.8, 136.6, 133.3, 128.4.

Mass : 275.

Anal. Calcd. for $C_7H_8N_{16}$: C, 26.28; H, 3.68; N, 40.87.

Found : C, 26.39; H, 3.60; N, 40.81.

***3-Amino-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate* *(4.9)*:** Yellow product (92 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 230 °C (dec.).



4.9

IR (KBr pellet, ν_{max}/cm^{-1}) : 3446, 3402, 3166, 1703, 1599, 1566, 1534, 1440, 1314, 1260, 1112, 953.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.03 (s, 1H), 8.85 (s, 1H), 7.73 (s, 1H).

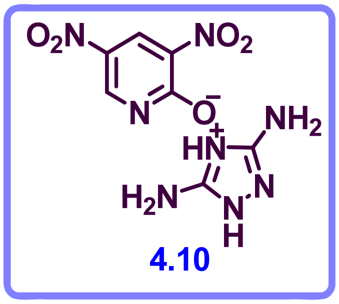
^{13}C NMR (100MHz, DMSO) : δ (ppm) 157.8, 155.9, 146.4, 145.3, 135.0, 132.3, 128.0.

Mass : 270.

Anal. Calcd. for $C_7H_7N_7O_5$: C, 31.23; H, 2.62; N, 36.42.

Found : C, 31.18; H, 2.74; N, 36.39.

3,5-Diamino-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate (4.10)**:** Yellow product (96 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 256 °C (dec.).



4.10

IR (KBr pellet, ν_{max}/cm^{-1}) **:** 3446, 3353, 3139, 2679, 1693, 1660, 1600, 1534, 1265, 1112, 1073, 1003, 942, 789, 712.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.05 (s, 2H), 8.07 (s, 1H), 8.06 (s, 1H).

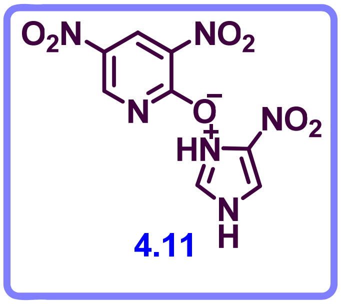
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.8, 153.8, 149.7, 133.0, 131.0, 127.6.

Mass : 285.

Anal. Calcd. for $C_7H_8N_8O_5$: C, 29.58; H, 2.84; N, 39.43.

Found : C, 29.48; H, 2.78; N, 39.51.

4-Nitro-1H-imidazol-3-ium 3,5-dinitropyridin-2-olate (4.11)**:** White product (95 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 305 °C (dec.).



4.11

IR (KBr pellet, ν_{max}/cm^{-1}) : 3139, 3073, 3018, 2870, 1692, 1615, 1555, 1511, 1429, 1363, 1308, 1248, 1139, 991.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.05 (s, 1H), 8.97 (s, 1H), 8.29 (s, 1H), 7.82 (s, 1H).

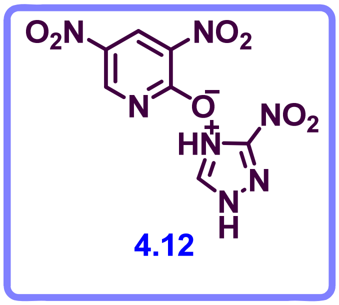
^{13}C NMR (100MHz, DMSO) : δ (ppm) 154.6, 147.9, 143.8, 136.5, 136.2, 133.4, 128.4, 119.4.

Mass : 299.

Anal. Calcd. for $C_8H_6N_6O_7$: C, 32.23; H, 2.03; N, 28.18.

Found : C, 32.14; H, 1.98; N, 28.11.

***3-Nitro-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate** (4.12)*: Yellow product (94 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 236 °C (dec.).



4.12

IR (KBr pellet, ν_{max}/cm^{-1}) : 3156, 3019, 2860, 1687, 1654, 1621, 1567, 1517, 1474, 1430, 1353, 1309, 1232, 1140, 981.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.0 (s, 2H), 8.9 (s, 1H), 8.8 (s, 1H).

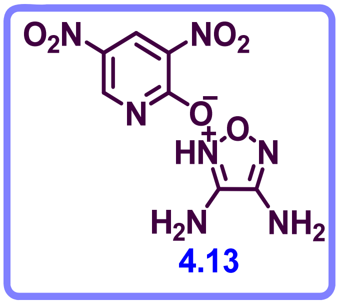
^{13}C NMR (100MHz, DMSO) : δ (ppm) 154.8, 146.5, 144.0, 139.0, 136.4, 133.3, 128.4.

Mass : 300.

Anal. Calcd. for $C_7H_5N_7O_7$: C, 28.10; H, 1.68; N, 32.77.

Found : C, 28.23; H, 1.56; N, 32.70

***3,4-Diamino-1,2,5-oxadiazol-2-ium 3,5-dinitropyridin-2-olate* *(4.13)*:** Yellow product (94 % yield). DSC-TGA (Heating rate: 10 °C min^{-1}): 267 °C (dec.).



4.13

IR (KBr pellet, ν_{max}/cm^{-1})	: 3430, 3320, 3265, 3194, 3085, 3013, 1693, 1648, 1621, 1572, 1533, 1473, 1424, 1358, 1303, 1232, 1139, 815.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 9.05 (s, 1H), 8.97 (s, 1H), 5.78 (s, 4H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 154.6, 150.1, 143.8, 136.6, 133.4, 128.4.
Mass	: 285.
Anal. Calcd. for $C_7H_7N_7O_6$	: C, 29.48; H, 2.47; N, 34.38.
Found	: C, 29.39; H, 2.40; N, 34.51.

4.5. References

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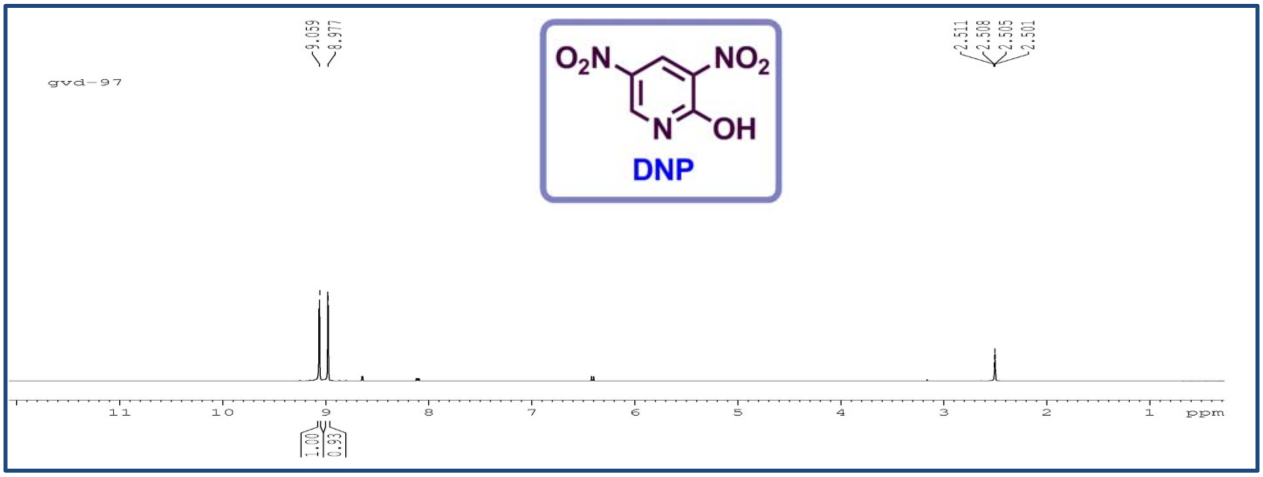


Figure 2.S1 *^{1}H NMR spectrum o 3,5-Dinitropyridin-2-ol (**DNP**).*

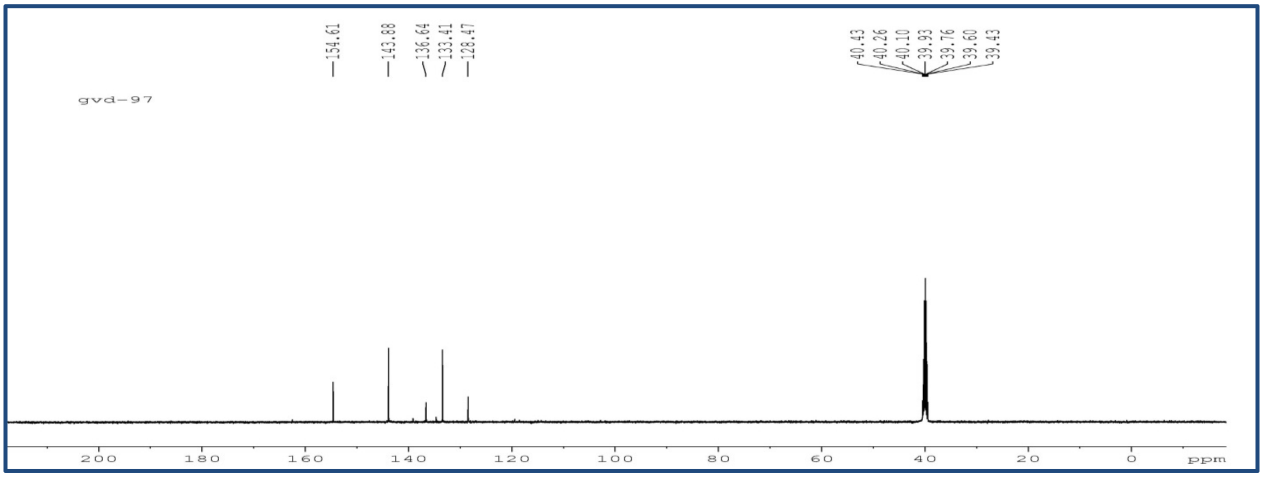


Figure 2.S2 *^{13}C NMR spectrum of 3,5-Dinitropyridin-2-ol (**DNP**).*

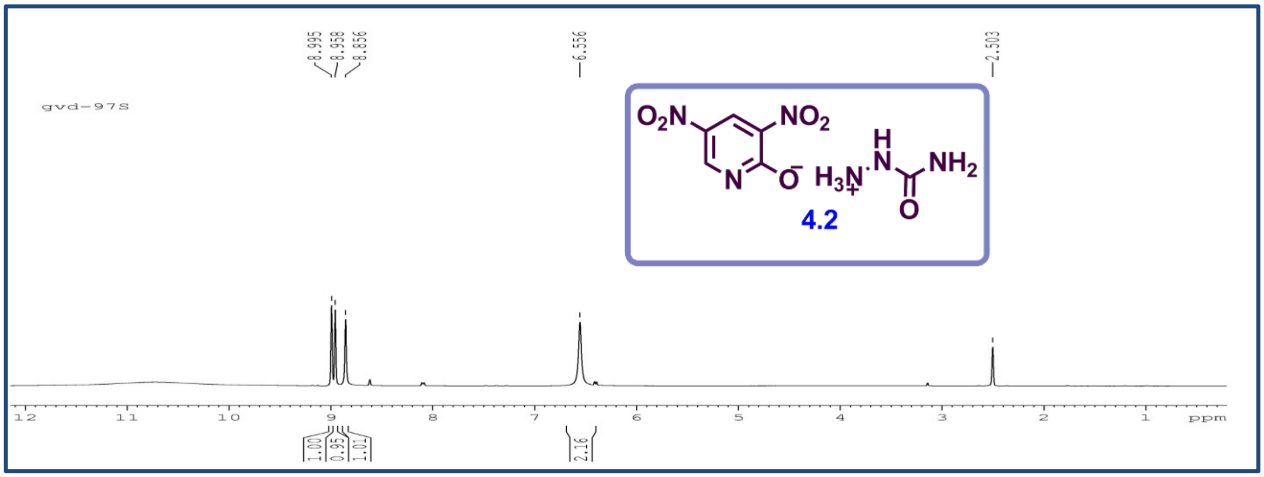


Figure 2.S3 *^{1}H NMR spectrum of Carbamoylhydrazinium 3,5-dinitropyridin-2-olate (**4.2**).*

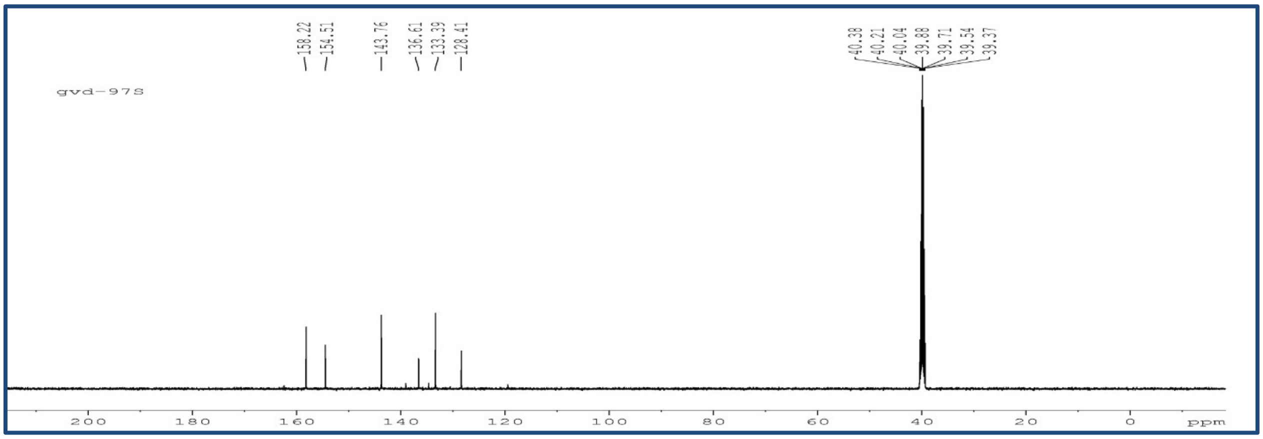


Figure 2.S4 ^{13}C *NMR spectrum of Carbamoylhydrazinium 3,5-dinitropyridin-2-olate (**4.2**)*

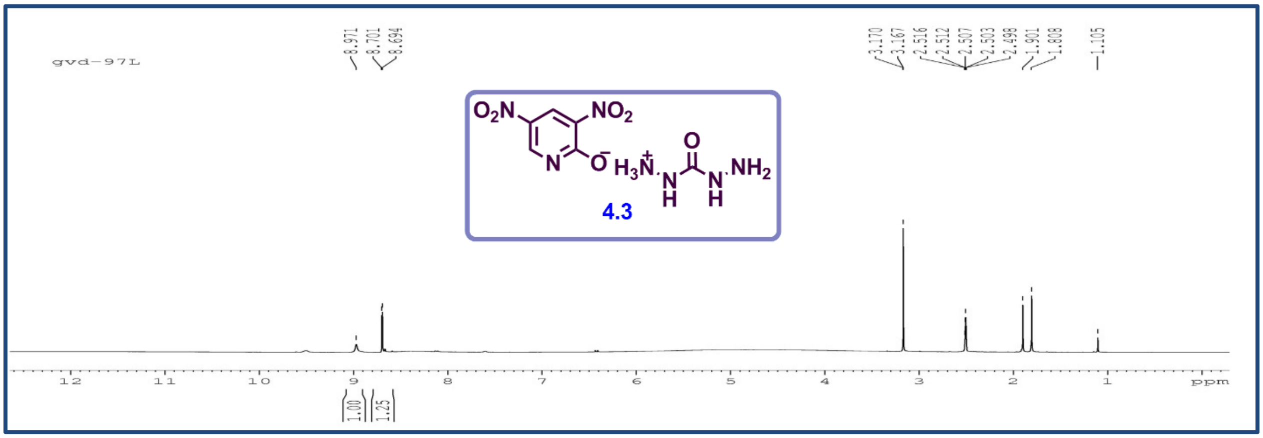


Figure 2.S5 ^{1}H *NMR spectrum of (Hydrazinylcarbonyl)hydrazinium 3,5-dinitropyridin-2-olate* ***(4.3)***.

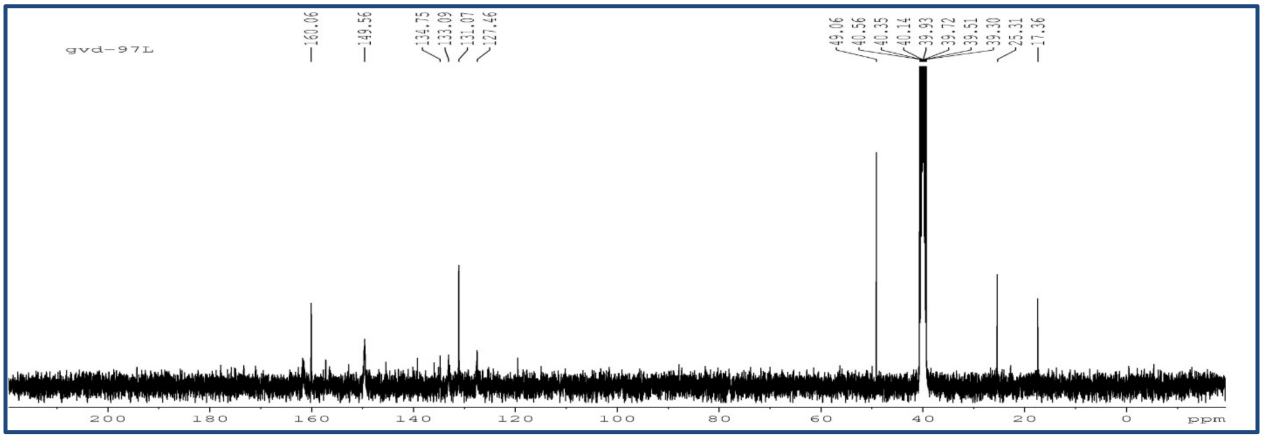


Figure 2.S6 ^{13}C *NMR spectrum of (Hydrazinylcarbonyl)hydrazinium 3,5-dinitropyridin-2-olate* ***(4.3)***.

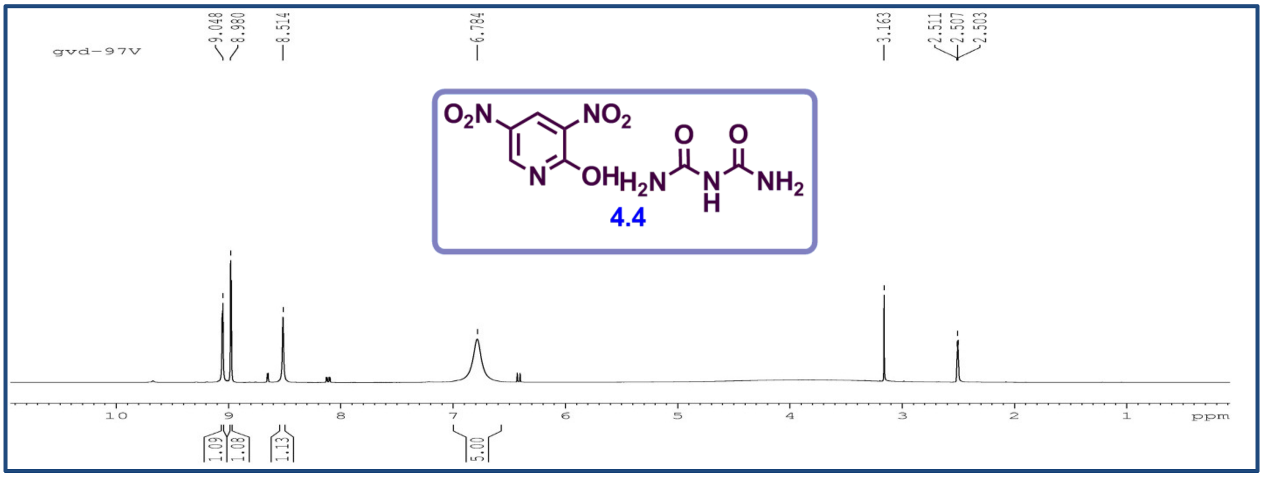


Figure 2.S7 *^{1}H NMR spectrum of Dicarbonimidic diamide-3,5-dinitropyridin-2-ol* ***(4.4)***.

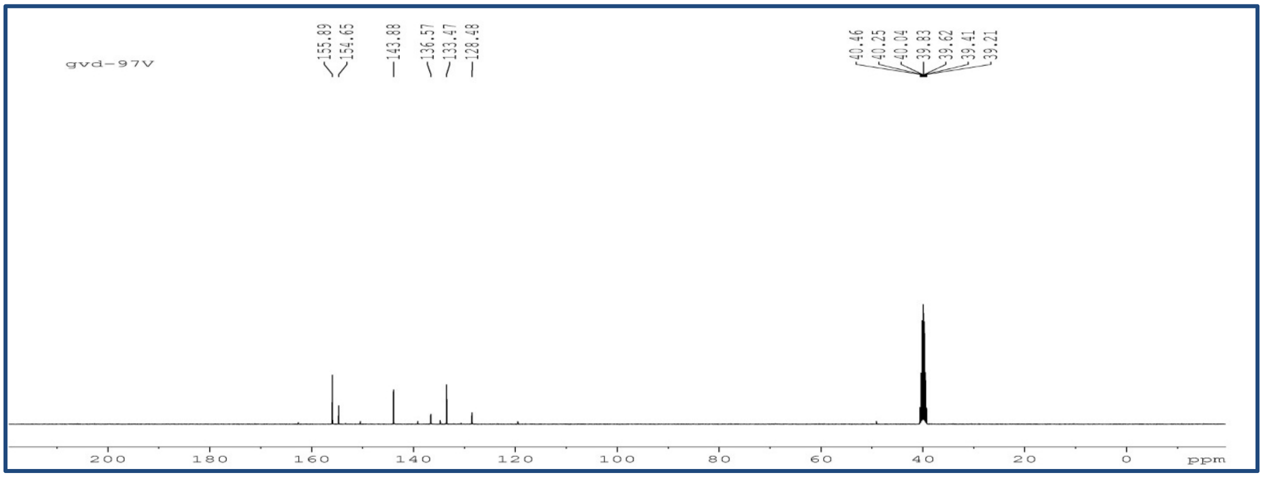


Figure 2.S8 *^{13}C NMR spectrum of Dicarbonimidic diamide-3,5-dinitropyridin-2-ol* ***(4.4)***.

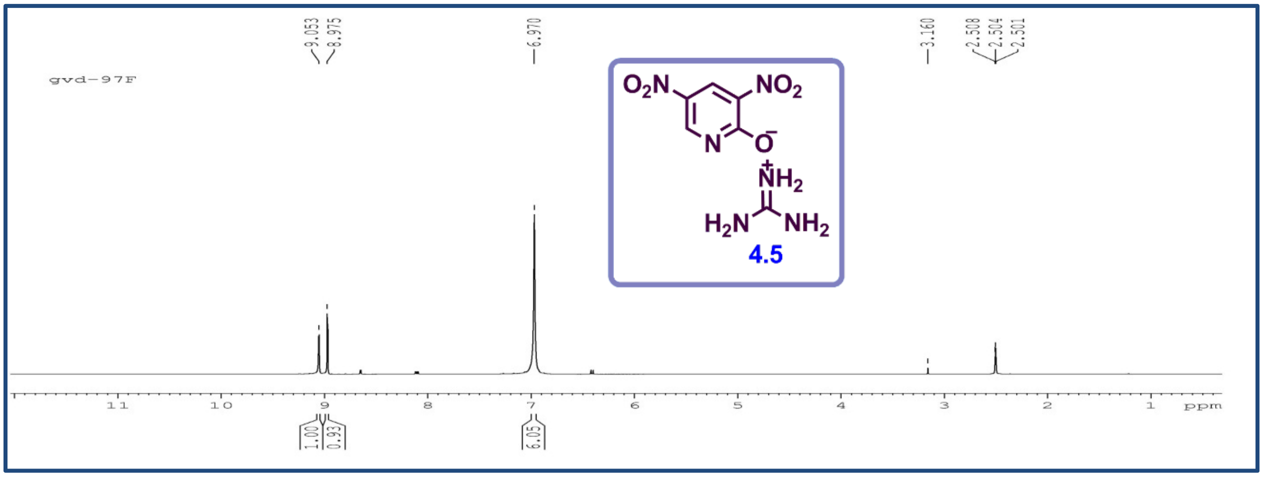


Figure 2.S9 *^{1}H NMR spectrum of Diaminomethaniminium 3,5-dinitropyridin-2-olate* ***(4.5)***.

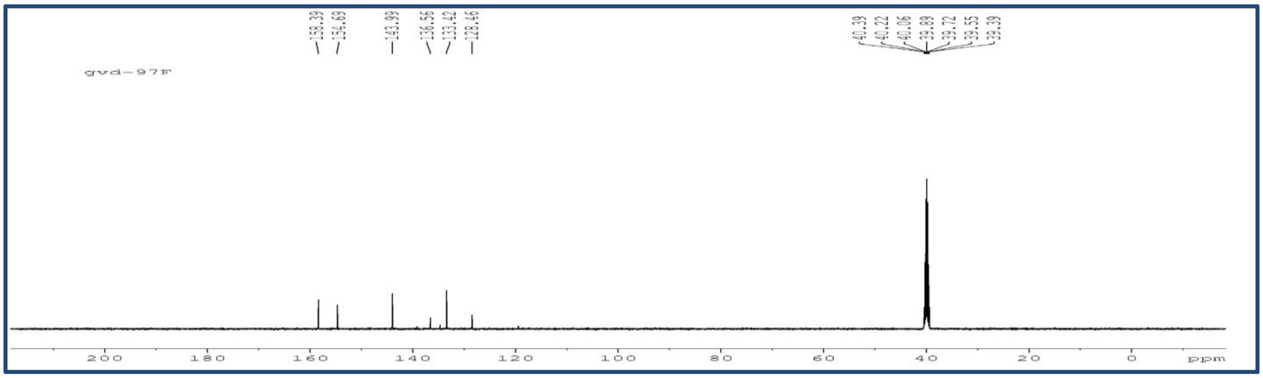


Figure 2.S10^{13}*C NMR spectrum of Diaminomethaniminium 3,5-dinitropyridin-2-olate* ***(4.5)***.

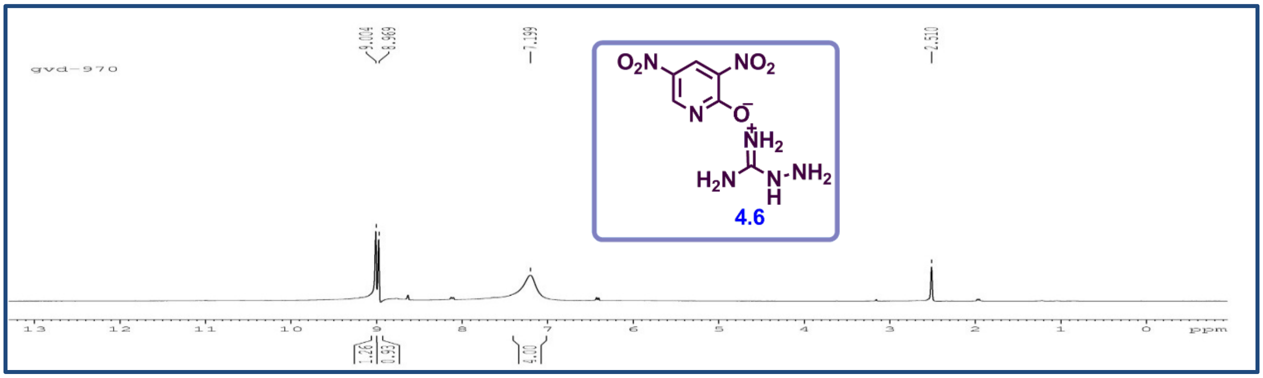


Figure 2.S11 ^{1}*H NMR spectrum of Amino(hydrazinyl)methaniminium 3,5-dinitropyridin-2-olate* ***(4.6)***.

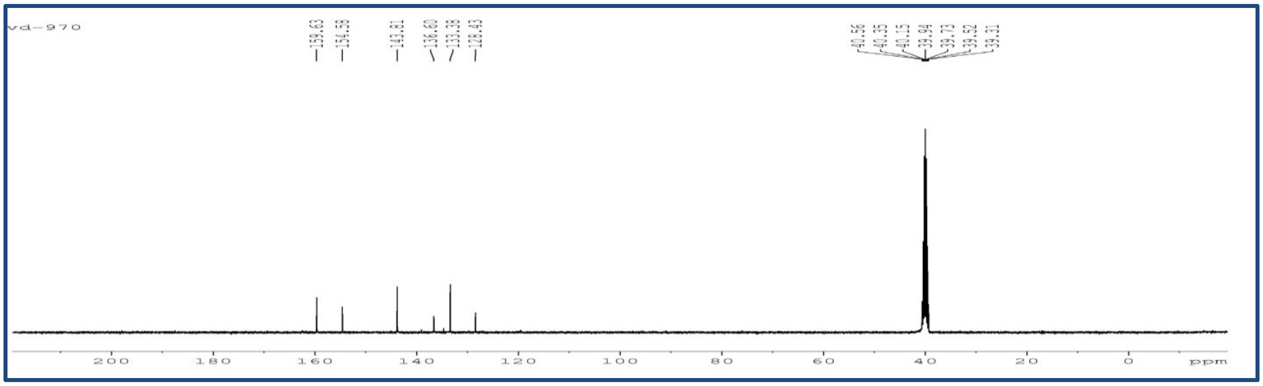


Figure 2.S12 ^{13}*C NMR spectrum of Amino(hydrazinyl)methaniminium 3,5-dinitropyridin-2-olate* ***(4.6)***.

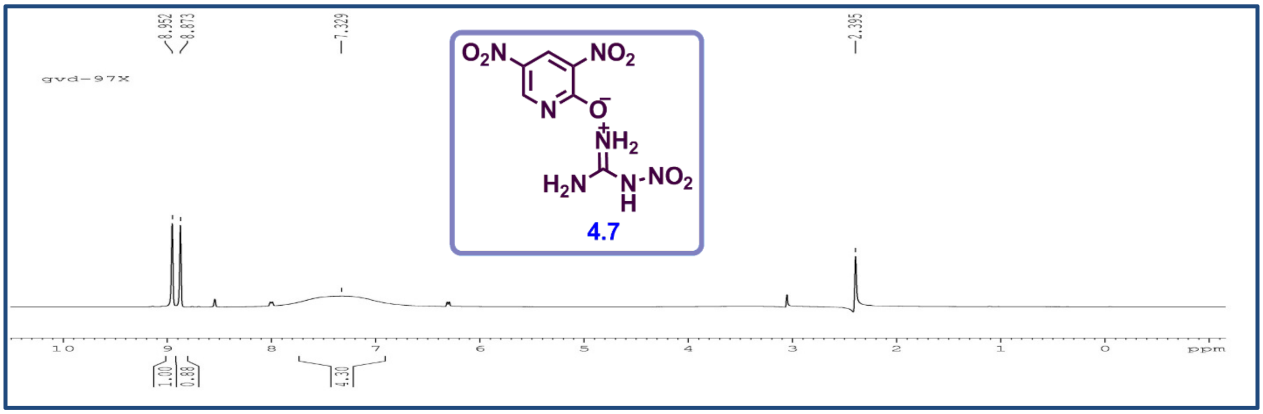


Figure 2.S13 *^{1}H NMR spectrum of Amino(nitroamino)methaniminium 3,5-dinitropyridin-2-olate* ***(4.7)***.

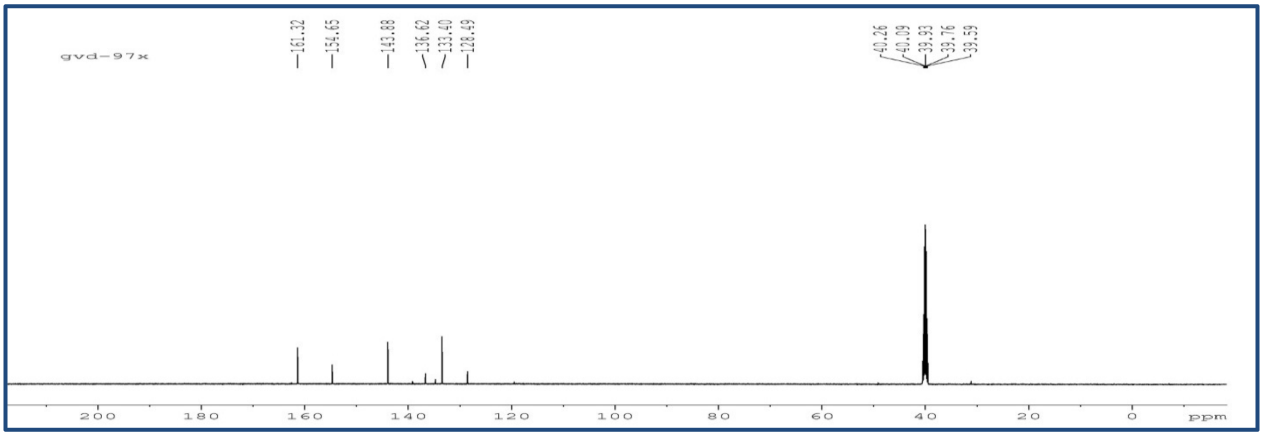
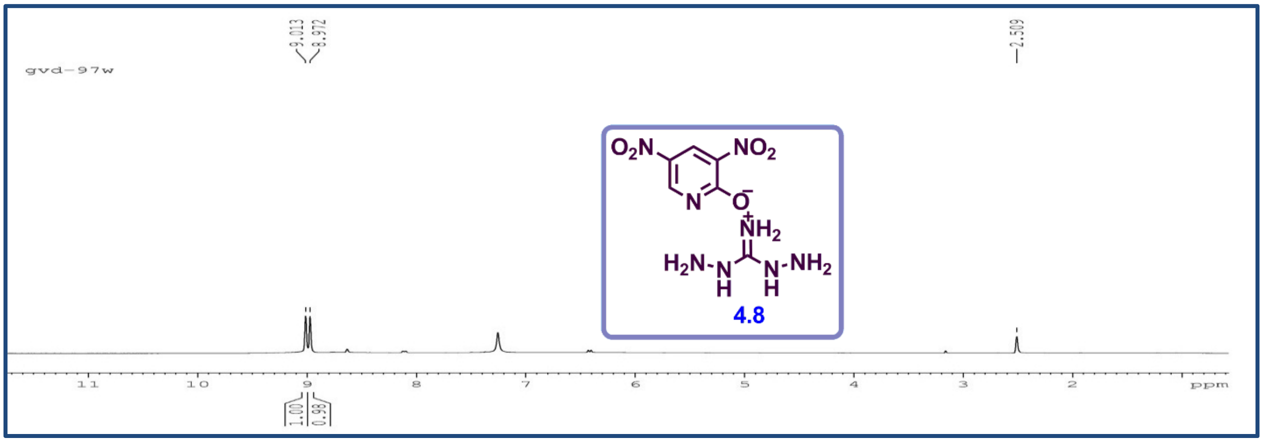


Figure 2.S14 *^{13}C NMR spectrum of Amino(nitroamino)methaniminium 3,5-dinitropyridin-2-olate* ***(4.7)***.



igure 2.S15 *^{1}H NMR spectrum of Dihydrazinylmethaniminium 3,5-dinitropyridin-2-olate* ***(4.8)***.

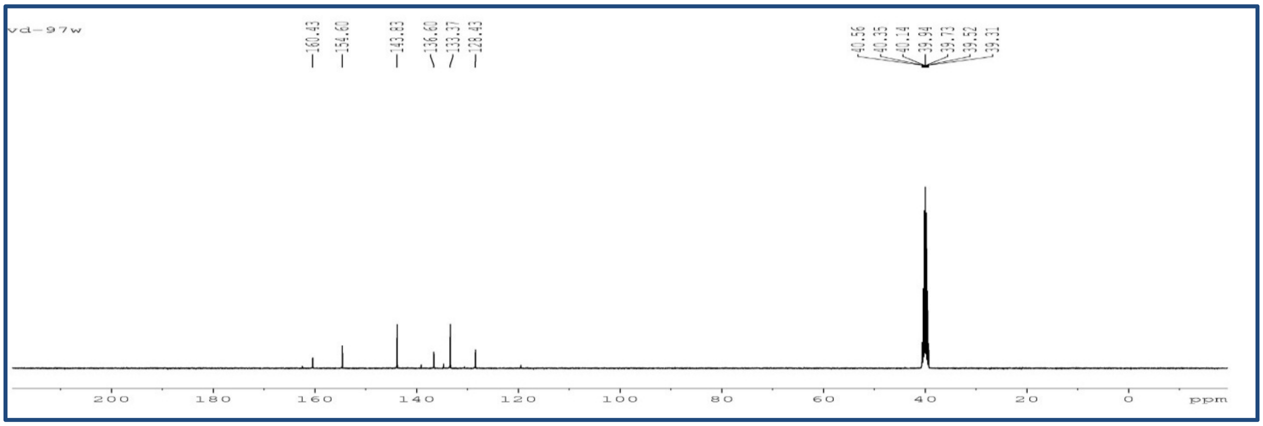


Figure 2.S16 *^{13}C NMR spectrum of Dihydrazinylmethaniminium 3,5-dinitropyridin-2-olate* ***(4.8)***.

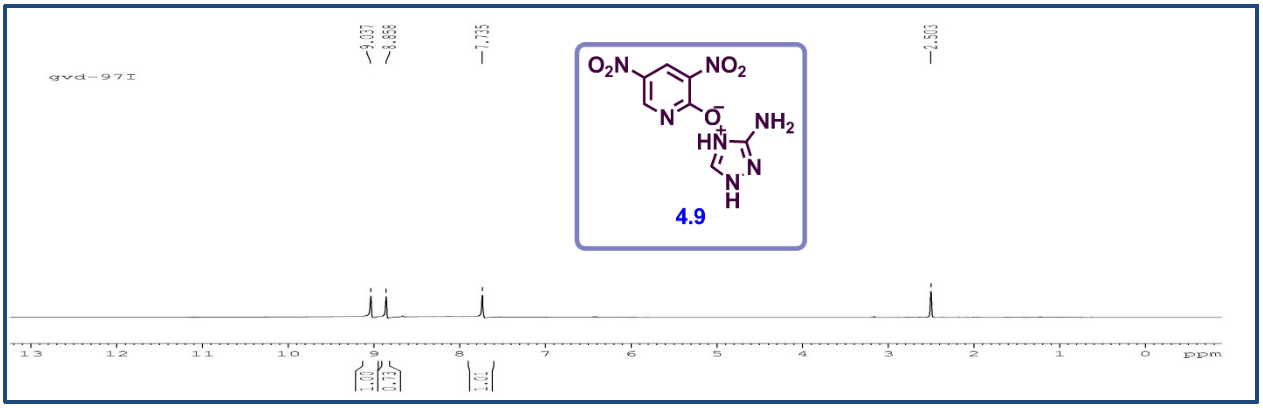


Figure 2.S17 *^{1}H NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate* ***(4.9)***.

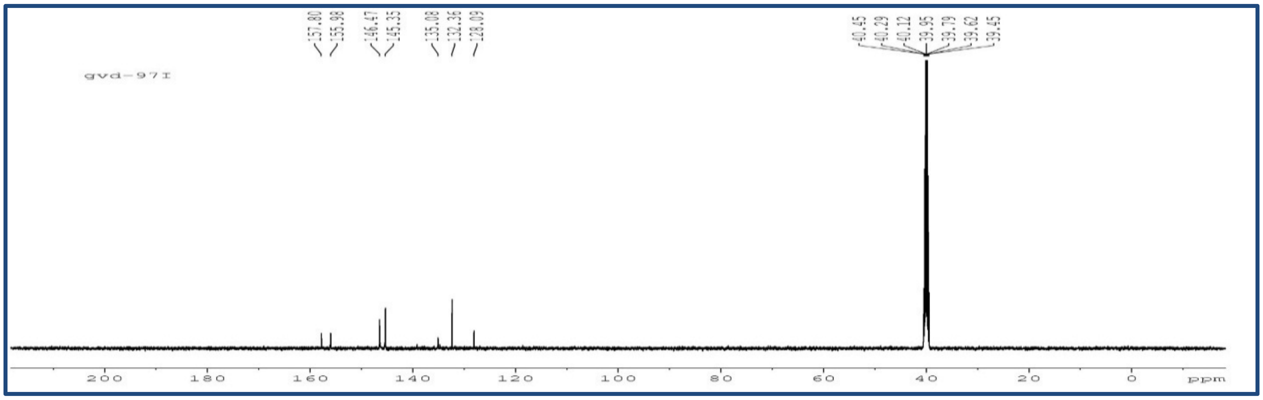


Figure 2.S18 *^{13}C NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate* ***(4.9)***.

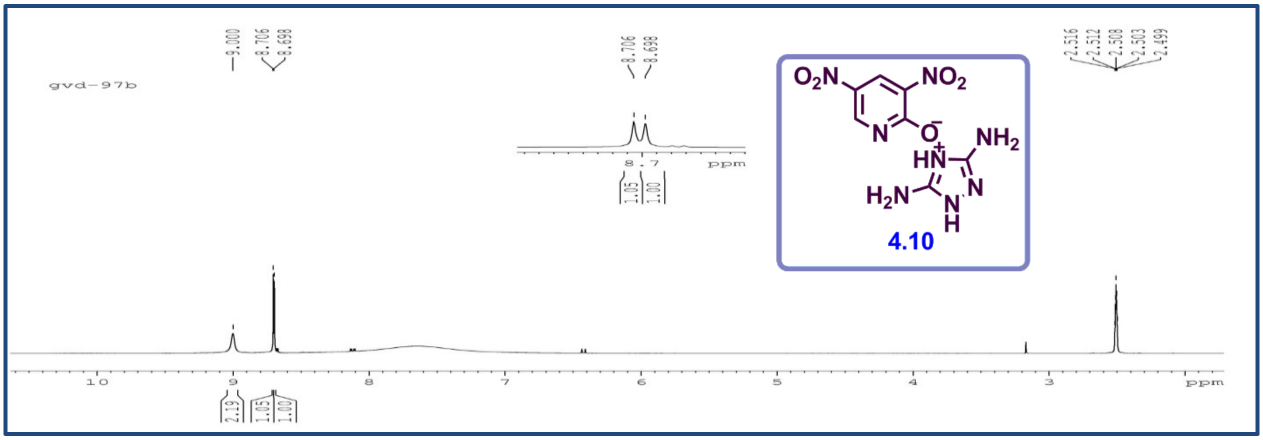


Figure 2.S19 *^{1}H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate* ***(4.10)****.*

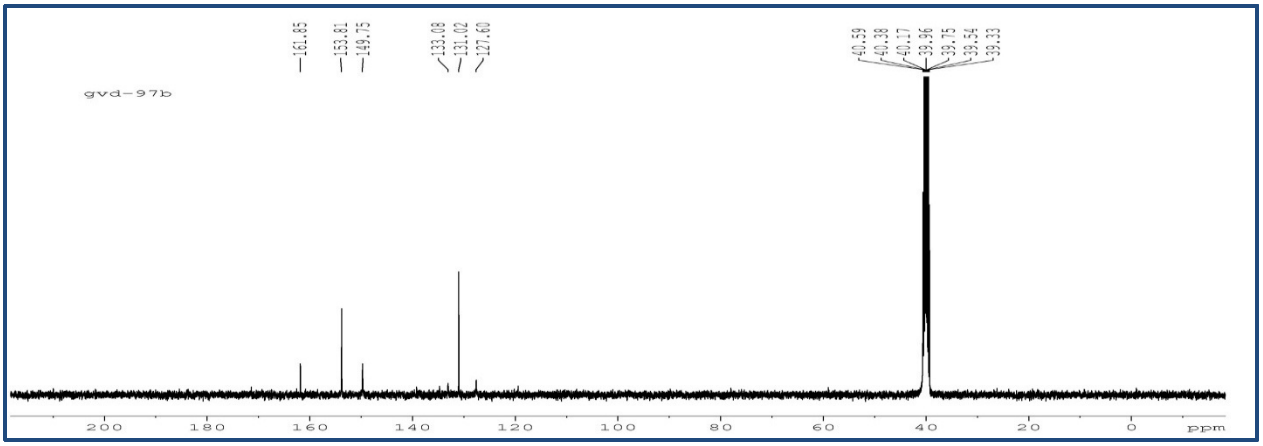


Figure 2.S20 *^{13}C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate* ***(4.10)****.*

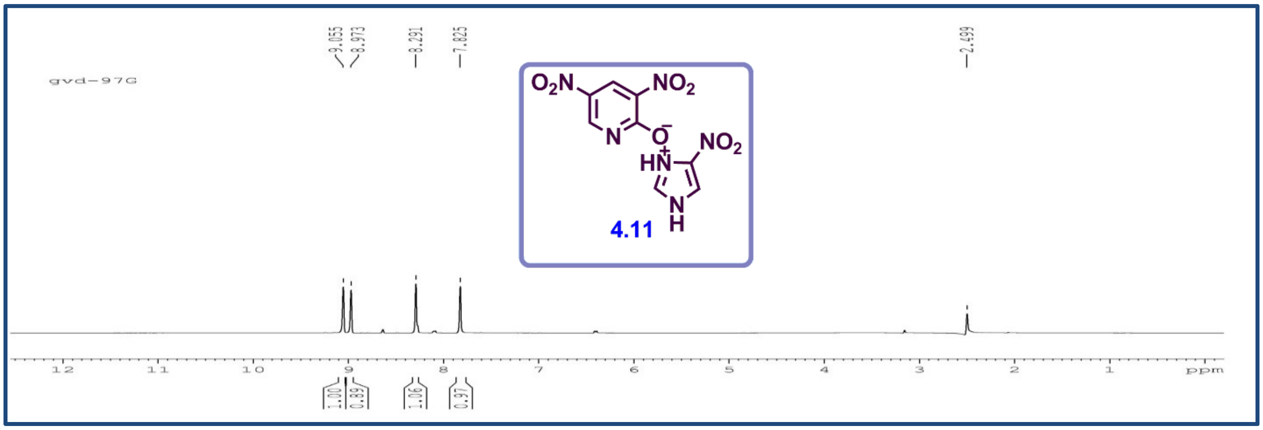


Figure 2.S21 *^{1}H NMR spectrum of 4-Nitro-1H-imidazol-3-ium 3,5-dinitropyridin-2-olate* ***(4.11).***

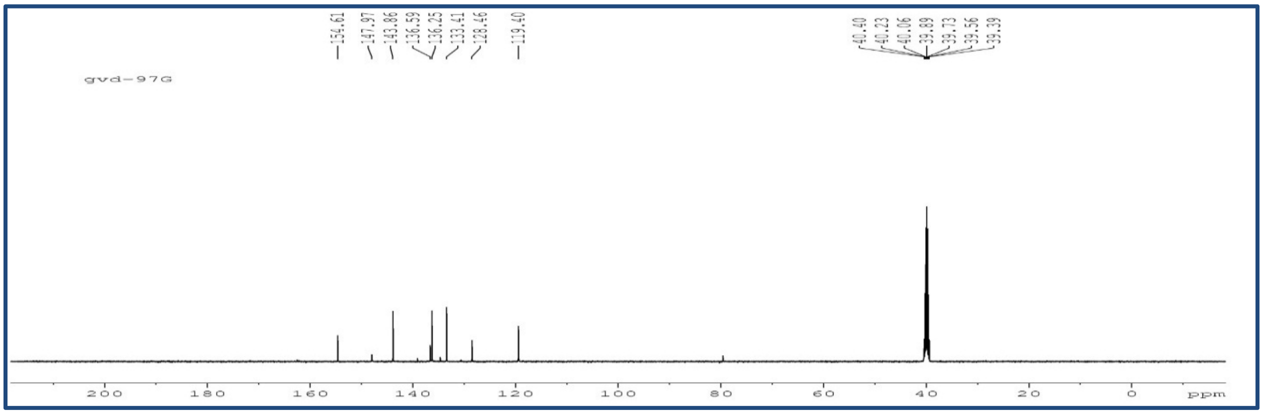


Figure 2.S22 ^{13}C NMR spectrum of 4-Nitro-1H-imidazol-3-ium 3,5-dinitropyridin-2-olate *(4.11)*.

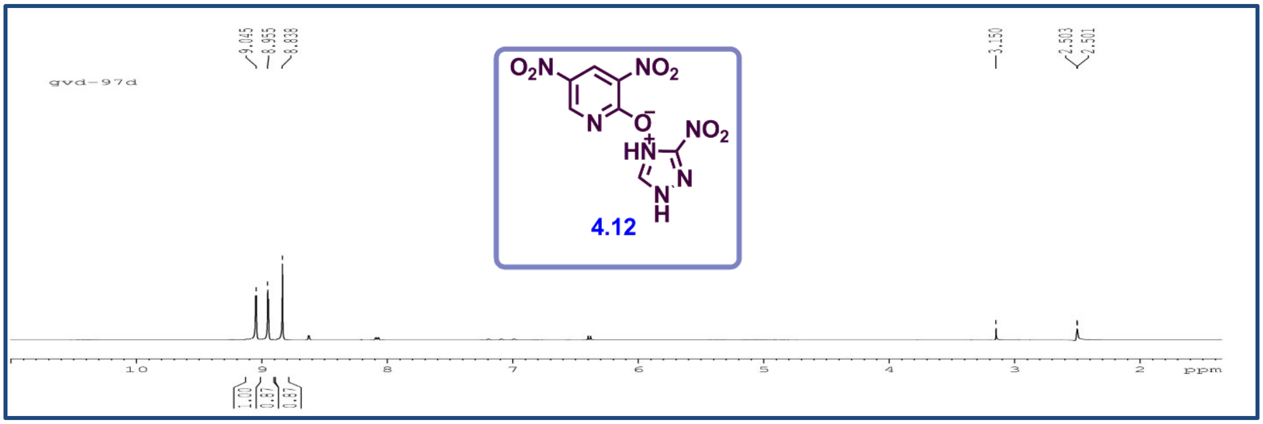


Figure 2.S23 ^{1}H NMR spectrum of 3-Nitro-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate *(4.12)*.

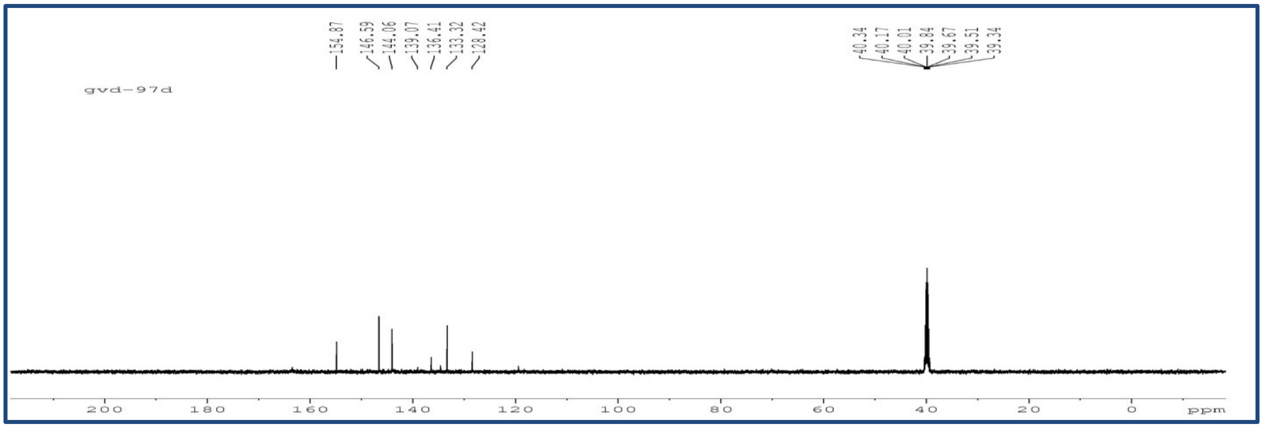


Figure 2.S24 ^{13}C NMR spectrum of 3-Nitro-1H-1,2,4-triazol-4-ium 3,5-dinitropyridin-2-olate *(4.12)*.

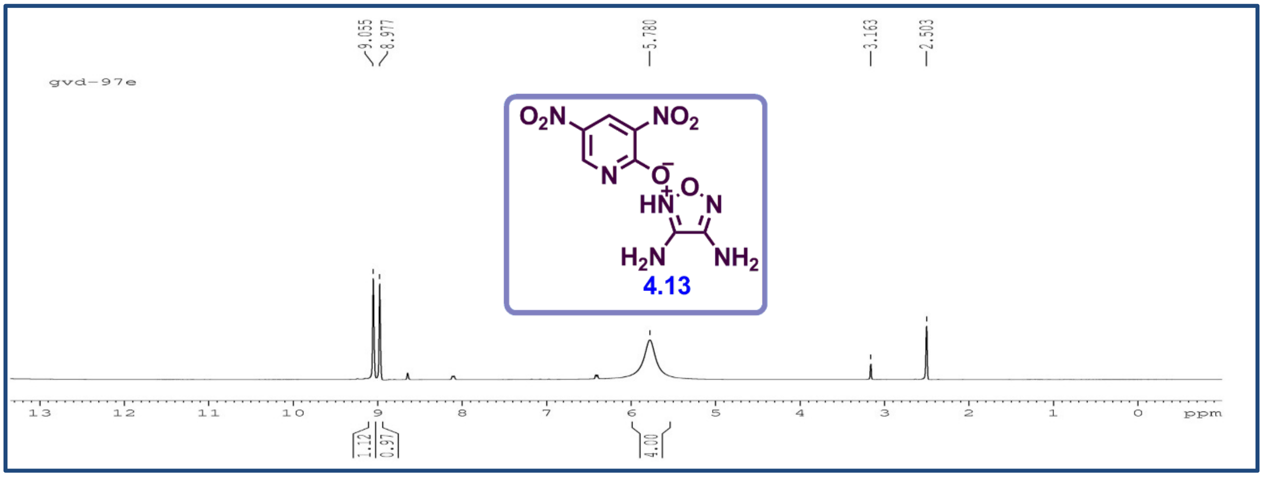


Figure 2.S25 *^{1}H NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 3,5-dinitropyridin-2-olate* ***(4.13)***.

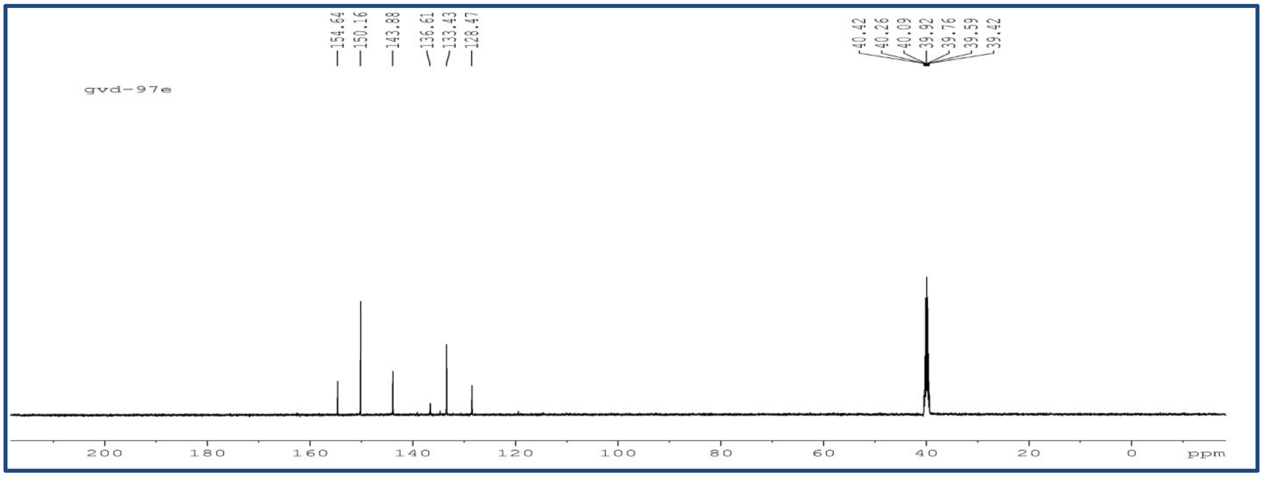


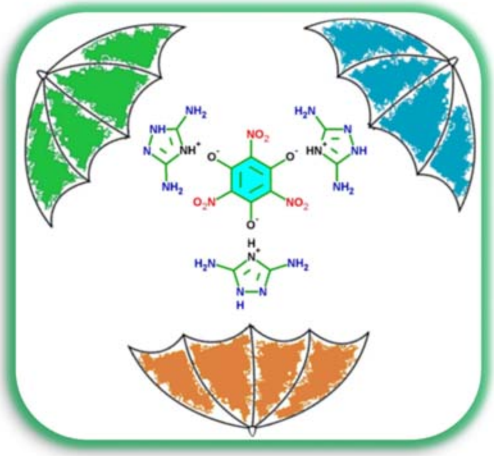
Figure 2.S26 *^{13}C NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 3,5-dinitropyridin-2-olate* ***(4.13)***.

CHAPTER 5

Energetic Salts Prepared from Phenolate Derivatives

Abstract

Several organic salts with **1:1, 2:1**, and **3:1** charge ratio (cation: anion) based on various cations and phenolate anions have been prepared. Their structures were characterized and confirmed by ^{1}H, ^{13}C NMR, DEPT spectroscopy, IR spectroscopy, MS and elemental analysis. Picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid, 2,4,6-trinitro-1,3,5-benzenetriol, and their salts were synthesized by a straightforward and simple method. Thermal stabilities were determined from thermo gravimetric differential thermal analysis (TG-DTA) measurements. Molecular structures of nitrophenols and their salts were investigated at the B3PW91/6-31G(d,p) level, and isodesmic reactions were designed for calculating the gas phase heats of formation. The solid state heats of formation for nitrophenols and selective nitrogen-rich heterocyclic compounds were calculated by the Politzer approach using heats of sublimation. Lattice potential energies and lattice energies for salts were predicted using Jenkins approach. Finally, the influence of nitrophenols, nitrogen-rich heterocyclic compounds and their salts on the energetic properties has been discussed.



5.1. Introduction

The enormous growth in the literature related to energetic salts since the year 2000 reflects their versatility, performance, controllable storage of energy and environmentally friendly properties in comparison to their starting materials [1]. Adding cations and anions with various functionalities to form energetic salts typically alters the energetic properties of individual starting materials, which is a desired characteristic of most of the energetic materials. Energetic salts possess several advantages over their atomically similar non-ionic analogs as these salts tend to exhibit lower vapour pressures and higher densities [2]. In recent years, the synthesis of energetic materials composed of heterocyclic compounds considerable interest due to their higher heats of formation, densities and oxygen balance than their hydrocarbon analogs [3]. The high positive heats of formation of these compounds are directly attributed to the large number of energetic N-N and C-N bonds in their molecular skeleton [4].

The chemistry of polynitroarenes have been widely studied and used in civil as well as military applications due to their remarkable properties [3,5]. Benzene compounds having three or more nitro groups, exhibit distinctly marked explosive properties (e.g. 2-methyl-1,3,5-trinitrobenzene (TNT), 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitroaniline (picramide) 2,4,6-trinitroanisole, 1,3-diammino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), etc.). Nitro group is an important source of oxygen in nitroarenes and most of these compound release energy mainly from the oxidation of hydrocarbon backbone. Thus, the combination of these compounds with heterocyclic compounds were expected to modify energetic properties. Previously, few salts of phenolate have been reported [6]. Salts of picric acid with ammonium, guanadinium, or heavy metal cations represented promising properties for applications in military charges and in initiating mixtures [7]. Nitrophenols have limited applications in energetic materials as they are known to react with surrounding metals to yield very sensitive compounds. Nitrophenols are also well known for salt formation and to stabilize the materials through the formation of hydrogen-bonded networks [8].

We have synthesized energetic salts based on picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid (2,4,6-trinitrobenzene-1,3-diol), and 2,4,6-trinitro-1,3,5-

benzenetriol, with concomitant determination of structural and thermal properties. We have extended our studies to understand structure-performance relationship with various cations in combination with phenolate anions having **1:1, 2:1** and **3:1** charge ratio. While the typical cations used in these systems are for example, 4-amino-4*H*-1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 3,4-diaminofurazan and guanidine, until now their phenolate salts have not been synthesized. In the field of energetic materials, these compounds have received much attention since they combine higher nitrogen content, higher enthalpy and lower sensitivity to external stimuli. Total energies, the zero-point energies, values of the thermal correction, gas phase heat of formation, molecular surface properties and calculated solid state heat of formation for the starting materials selected for salt preparation. They can form all kinds of salts with inorganic and organic acids due to the alkaline nature of these compounds. These salts have wide applications in propellants, secondary explosives and gas generator compositions. Further, it is necessary to study the influence of hydroxyl and nitro groups on the physicochemical properties of its salts systematically and to understand what characteristics make salts suited to high energy materials applications.

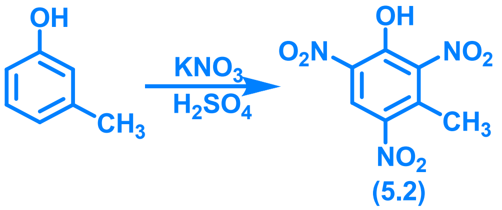
5.2. Results and discussion

5.2.1. Synthesis and characterization

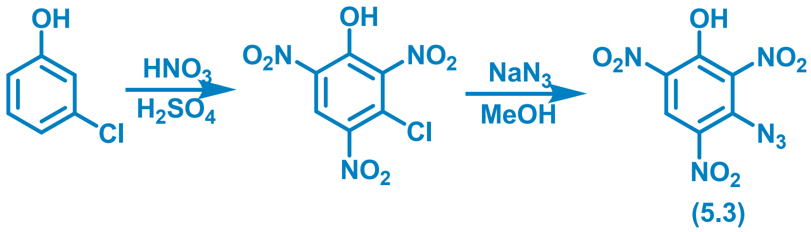
To meet the continuing need for high performance energetic materials with improved properties, the synthesis of materials containing heterocyclic compounds has gained considerable attention because of their high nitrogen content, large densities, good oxygen balances and high heats of formation. Energetic salts of nitrophenols are interesting as a new class of ionic energetic materials since they have good thermal stabilities, high densities, good oxygen balances and good performances. Their syntheses are feasible to scale-up through straightforward synthetic routes. The variations of nitro groups on phenol rings also have a significant influence on their microstructures and physicochemical properties [9]. We have mainly chosen trinitrophenols due to their stronger acidity than phenol and it is also necessary to study the influence of nitro groups on the structure-performance relationship of nitrophenol salts systematically. The acidity of nitrophenols arises from the greater resonance stabilization of phenoxide anion compared with phenol itself.

The synthesis of picric acid was achieved by nitration of 2,4-dinitrophenol using concentrated H_2SO_4 and HNO_3. The nitration of m-cresol using sulfuric acid and nitric acid resulted in vigorous reaction and hence, we attempted nitration using potassium nitrate and sulfuric acid to give 2,4,6-trinitro-m-cresol with excellent yield (scheme 5.1). We observed that nitration using KNO_3 was convenient and efficient for multiple nitrations in a single step. Generally, trinitrations needs more vigorous reaction conditions than mono- or dinitrations. However, in the case of picric acid the strong nitration mixture promoted oxidative decomposition of starting substrate, intermediates and products which led to poor yields. It is worth mentioning here is that sulfuric acid solutions of nitrate salts like $NaNO_3$, KNO_3 and NH_4NO_3 were once widely used as nitrating agents but eventually lost popularity in favor nitration mixture [10].

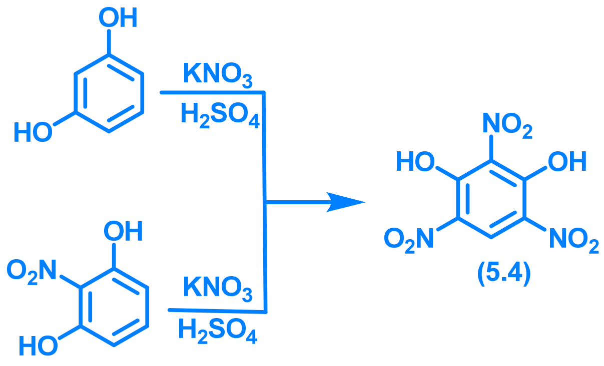
Nitration of 3-chlorophenol with nitrating agents (Scheme 5.2) gives 3-chloro-2,4,6-trinitrophenol. The displacement of the chlorine of 3-chloro-2,4,6-trinitrophenol by azide occurred to give 3-azido-2,4,6-trinitrophenol. The nitration of 3-chlorophenol with KNO_3 results in 3-chloro-2,4-dinitrophenol, however, we paid attention to trinitro derivatives of phenols. Next similar successful attempts were made to prepare styphnic acid and 2,4,6-trinitrophloroglucinol with good yields and their salts were obtained in high yield (Scheme 5.3 and 5.4). The choice of the nitrate salt ($NaNO_3$ and KNO_3) had minor effects on the yields of trinitrations of resorcinol and phloroglucinol. The new energetic salts (**5.1a-5.1e**) were easily obtained by reacting picric acid with an equivalent amount of heterocyclic cationic molecules in methanol (Scheme 5.5). All salts of nitrophenols prepared in methanol at room temperature, while the reaction of 3-azido-2,4,6-trinitrophenol (**5.3**) and styphnic acid (**5.4**) with 4-amino-4H-1,2,4-triazole (**a**) did not occur under similar conditions; hence, the corresponding salts (**5.3a** and **5.4a**) could not be prepared by this route. Scheme 5.5 represents the different anionic and cationic compounds selected in salt preparation. The structures of nitrophenols and their salts were characterized by ^{1}H, ^{13}C NMR, DEPT, IR, MS as well as elemental analysis.



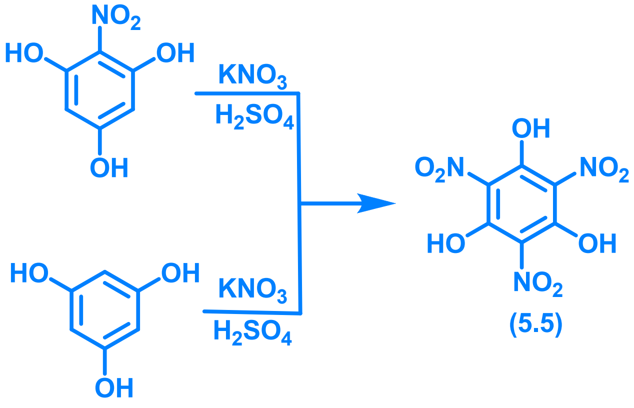
Scheme 5.1. Synthesis of 2,4,6-trinitro-m-cresol.



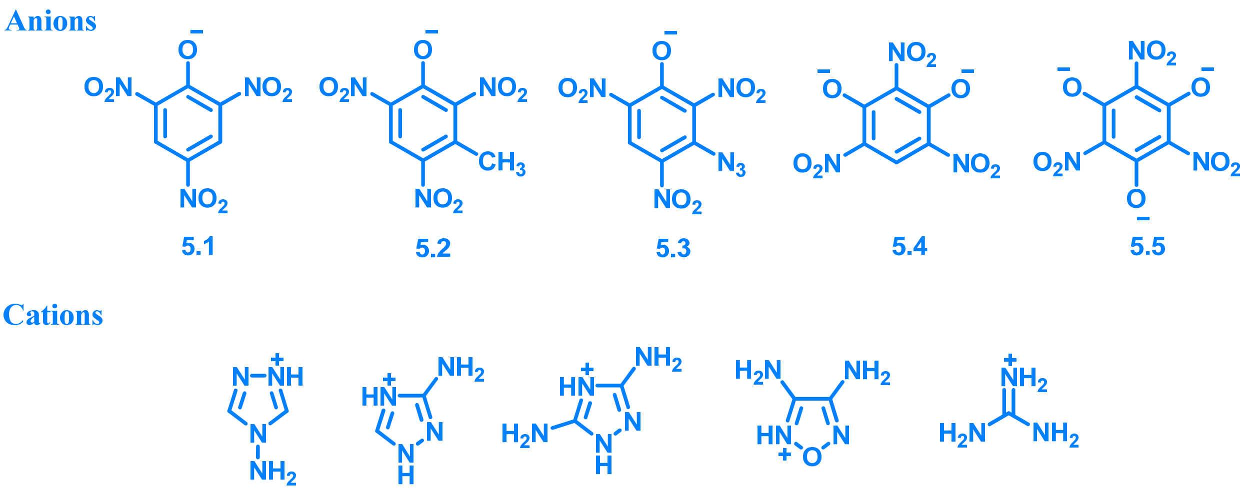
Scheme 5.2. Synthesis of 3-azido-2,4,6-trinitrophenol.



Scheme 5.3. Synthesis of styphnic acid.



Scheme 5.4. Synthesis of 2,4,6-trinitrophloroglucinol.



Scheme 5.5. Synthesis of energetic salts from nitrophenolate derivatives.

5.2.2. Thermal stabilities and energetic properties

The most fundamental performance properties of a potentially energetic compound are the heat of formation (HOF), density, chemical energy of detonation (Q), detonation velocity (*VOD*) and detonation pressure (*DP*). The gas phase HOFs of molecules were obtained from the isodesmic reactions.

The enthalpies of formation of high energy materials depend on the molecular skeleton of that compound. As a result, nitrogen-rich heterocycles, especially triazole, showed higher heats of formation (192 $kJmol^{-1}$) [11]. Increasing the number of nitrogen atoms in heterocycles resulted in considerable gain in the standard heat of formation in the resulting compounds. Comparing the heats of formation of phenol (-96 $kJmol^{-1}$) [12], m-cresol (-133 $kJmol^{-1}$) [12], resorcinol (-284 $kJmol^{-1}$) [13] and phloroglucinol (-452 $kJmol^{-1}$) [14] clearly reveal no significant energy contribution from these molecules and tend to reduce the overall HOF. In case of two –OH groups in phenol reduce the HOF of phloroglucinol by ~350 $kJmol^{-1}$. Adding one methyl ($-CH_3$) group to picric acid slightly decreases the HOF of 2,4,6-trinitro-m-cresol, while insertion of two –OH groups in phenol reduce the HOF of phloroglucinol by ~350 $kJmol^{-1}$. Adding one methyl ($-CH_3$) group to picric acid slightly decreases the HOF of 2,4,6-trinitro-m-cresol, while insertion of azido (-N_3) in picric acid group significantly improves the HOF of 3-azido-2,4,6-trinitrophenol to positive (Table 5.1).

Table 5.1. Energetic properties of nitrophenols.

Compd	OB[a]	HOF[b]	ρ[c]	*VOD*[d]	DP[e]	T_{dec}[f]	Mp[g]
Picric acid (5.1)	**-45.4**	**-268.44 (-218)[18]**	**1.77 (1.77)**	**7.50 (7.35)[7]**	**24.68 (23.2)[17]**	**242**	**120**
2,4,6-Trinitro-m-cresol (5.2)	**-62.6**	**-296.14**	**1.69 (1.68)[7]**	**7.08 (6.85)[7]**	**21.39**	**212**	**106**
3-Azido-2,4,6-trinitrophenol (5.3)	**-35.6**	**26.26**	**1.84**	**7.94**	**28.31**	**254**	**86**
Styphnic acid (5.4)	**-35.9**	**-485.42 (-468, -523)[19,20]**	**1.79 (1.83)[7]**	**7.51**	**24.90**	**190**	**173**
2,4,6-Trinitro-1,3,5-benzenetriol (5.5)	**-27.6**	**-654.07**	**1.81**	**7.58 (8.05)[18]**	**25.59 (27.56)[18]**	**191**	**166**

[a] Oxygen balance (%). [b] Heat of formation in solid state (kJmol^{-1}). [c] Density (gcm^{-3}). [d] Velocity of detonation (kms^{-1}). [e] Detonation pressure (GPa). [f] Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [g] Melting point (°C).

The calculated energetic properties of the nitrophenols are summarized in Table 5.1. As evident from Table 5.2, replacement of 3-amino-1,2,4-triazole with 3,5-diamino-1,2,4-triazole reduces the HOF of corresponding salts. However, we observed that 4-amino-4*H*-1,2,4-triazole significantly improves the HOF of its related salts. HOF of 4-amino-4*H*-1,2,4-triazole is the highest among a series of heterocyclic compounds selected and hence its salts possess highest HOFs in different series of compounds. Guanidine show negative HOF and hence, has very less impact on their energetic salts. Among the series of nitrophenol salts, the salts of 3-azido-2,4,6-trinitrophenol (**5.3b-5.3e**) possess highest HOFs attributed to the presence of azido group.

Density is one of the most important physical properties of energetic materials. The Hofmann approach [15] is used to predict the densities of ionic materials from its volume and the molecular mass. The densities of most of the new salts ranged between

1.58 and 1.76 gcm^{-3}. The presence of nitro groups and N-H in the molecular framework increased the opportunity for hydrogen bonding and may responsible for the increased densities in the designed compounds. Introduction of $–CH_3$ group in parent picric acid reduced the density and similar trend is observed in salts of picric acid (**5.1a-5.1e**) and 2,4,6-trinitro-m-cresol (**5.2a-5.2e**). However, introduction of $–N_3$ group in picric acid improves the density and similar can be seen in salts of picric acid (**5.1a-5.1e**) and 3-azido-2,4,6-trinitrophenol (**5.3b-5.3e**). Replacement of 3-amino-1,2,4-triazole with 3,5-diamino-1,2,4-triazole show marginal change in density. Among the energetic salts, guanidine containing salts possessed lower densities.

The detonation performance of an energetic compound is basically depending on the density, the heat of formation and the oxygen balance. By using the calculated values of the HOFs and densities of the energetic nitrophenols and their salts, the detonation velocities and detonation pressures were calculated based on Kamlet-Jacobs equations. In the present study, the designed compounds composed only of the atoms C, H, N and O and hence, N_2(g), H_2O(g), CO_2(g) and C(s) are assumed as important detonation products, explained by Kamlet et al [16]. and Politzer and Murray [17].

Table 5.2. *Energetic properties of picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid and 2,4,6-trinitro-1,3,5-benzenetriol salts.*

Compd.	**OB**[a]	**HOFc**[b]	**HOFa**[c]	U_{Pot}[d]	H_L[e]	HOF_{salt}[f]	**ρ**[g]	**VOD**[h]	**DP**[i]	**Q**[j]	T_{dec}[k]	**Mp**[l]
5.1a	-63.9	946.92	-458.31	465	471	18	1.68	7.21	22.08	1186	240	192
5.1b	-63.9	796.42	-458.31	465	471	-132	1.68	7.02	20.98	1071	--	231
5.1c	-63.4	753.78	-458.31	458	463	-168	1.67	6.96	20.54	1012	254	241
5.1d	-55.9	849.56	-458.31	460	465	-74	1.70	7.37	23.29	1204	238	112
5.1e	-61.1	567.16	-458.31	475	479	-371	1.66	6.94	20.32	984	291	120
5.2a	-75.8	946.92	-457.17	455	460	29	1.63	6.96	20.20	1176	225	175
5.2b	-75.8	796.42	-457.17	455	460	-121	1.63	6.79	19.23	1066	225	185
5.2c	-74.9	753.78	-457.17	449	454	-157	1.63	6.76	19.08	1009	235	206
5.2d	-67.6	849.56	-457.17	451	456	-63	1.65	7.13	21.35	1194	211	103
5.2e	-74.2	567.16	-457.17	464	468	-359	1.60	6.67	18.35	984	175	107
5.3b	-54.2	796.42	-143.59	453	458	194	1.74	7.43	24.02	1152	191	119
5.3c	-54.2	753.78	-143.59	447	452	158	1.73	7.37	23.52	1096	210	--
5.3d	-47.6	849.56	-143.59	448	454	252	1.76	7.74	26.23	1267	198	78
5.3e	-51.1	567.16	-143.59	462	466	-43	1.72	7.38	23.49	1084	156	--
5.4b	-67.8	796.4	-523.4	1281	1289	-220	1.66	6.79	19.44	927	227	--
5.4c	-66.8	753.8	-523.4	1253	1261	-277	1.65	6.71	18.95	858	248	--
5.4d	-55.7	849.6	-523.4	1261	1268	-93	1.69	7.35	23.05	1140	219	146
5.4e	-63.9	567.2	-523.4	1320	1328	-717	1.61	6.49	17.43	757	199	--
5.5a	-70.2	946.9	-203.5	2238	2247	389	1.64	7.17	21.50	1164	196	--
5.5b	-70.2	796.4	-203.5	2238	2247	-62	1.64	6.82	19.46	954	223	147
5.5c	-68.8	753.8	-203.5	2176	2186	-128	1.63	6.74	18.97	877	202	--
5.5d	-55.6	849.6	-203.5	2193	2203	143	1.68	7.49	23.87	1211	182	--
5.5e	-65.8	567.2	-203.5	2325	2335	-837	1.58	6.43	16.89	731	170	--

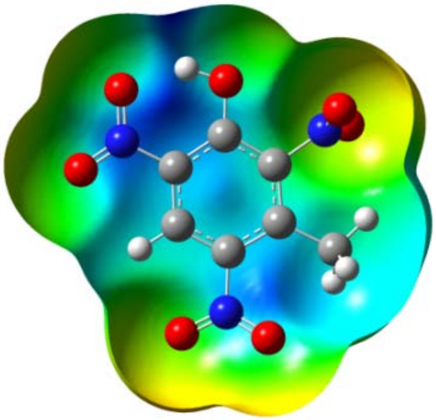
[a] Oxygen balance (%). [b] Heat of formation of cation (kJmol^{-1}). [c] Heat of formation of anion ((kJmol^{-1}). [d] Lattice potential energy ((kJmol^{-1}). [e] Lattice energy (kJmol^{-1}). [f] Heat of formation of salt ((kJmol^{-1}). [g] Density (gcm^{-3}). [h] Velocity of detonation (kms^{-1}). [i] Detonation pressure (GPa). [j] Chemical energy of detonation (calg^{-1}). [k] Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C/min). [l] Melting point (°C).

The predicted detonation characteristics of picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid and 2,4,6-trinitrophloroglucinol listed in Table 5.1 and found close agreement with experimental data. The calculated detonation pressures of picric acid salts (**5.1a-5.1e**), styphnic acid (**5.4b-5.4e**) and 2,4,6-trinitrophloroglucinol (**5.5a-5.5e**) lie in the range between *DP*=16.8 and *DP*=24 GPa and detonation velocities lie between *VOD*=6.4 and *VOD*=8 km/s. Comparing the performance characteristics of 2,4,6-trinitro-m-cresol (**5.2a-5.2e**) and 3-azido-2,4,6-trinitrophenol (**5.3b-5.3e**) salts reveals that 3-azido-2,4,6-trinitrophenol salts possess better performance due to their high densities. The formal replacement of 2,4,6-trinitro-m-cresol's methyl group by a hydroxyl group, as in the parent styphnic acid, results in detonation parameters better than those of 2,4,6-trinitro-m-cresol. Among the nitrophenol salts, 3,4-diaminofurazan salts show better detonation performance and these performance properties coupled with the better thermal stabilities make these salts attractive candidates for energetic materials.

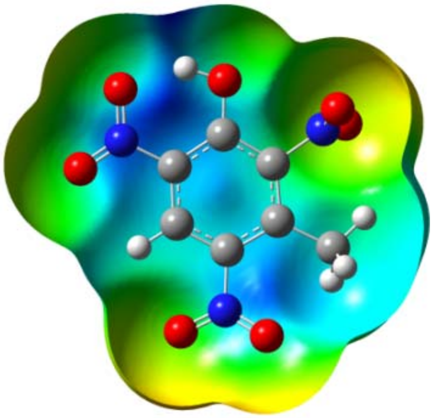
For energetic materials, stability and physical properties are very important. The melting points and the decomposition temperatures of nitrophenol salts were obtained by using TG-DTA from a heating rate of 10 °C/min and corresponding values are listed in Table 2. As shown in Table 2, for salts **5.1a-5.1e** in which the picric acid anion is present, all salts appear to be sufficiently thermally stable, their decomposition temperatures found in the range 231-291 °C, while their melting points lie between 110-241 °C. Salt **5.1b** observed to decompose without melting above 230 °C. All the picric acid salts have melting points greater than 100 °C. Similar to picric acid salts, styphnic acid salts (**5.4b-5.4e**) and 2,4,6-trinitro-1,3,5-benzenetriol salts (**5.5a-5.5e**) exhibit better thermal stabilities. Styphnic acid and 2,4,6-trinitro-1,3,5-benzenetriol salts shows decomposition temperatures above 190 and 170 °C, respectively. Among the 2,4,6-trinitro-m-cresol salts, **5.2a, 5.2b** and **5.2c** have decomposition temperature above 220 °C with high melting points (>170 °C). 3-Azido-2,4,6-trinitrophenol salts possess decomposition temperature above 150 °C. The experimental results show that with the increase of nitro groups in the phenol rings, the amount of releasing heat increase, which are beneficial to improve the performance of energetic organic salts.

5.2.3. Molecular electrostatic potential

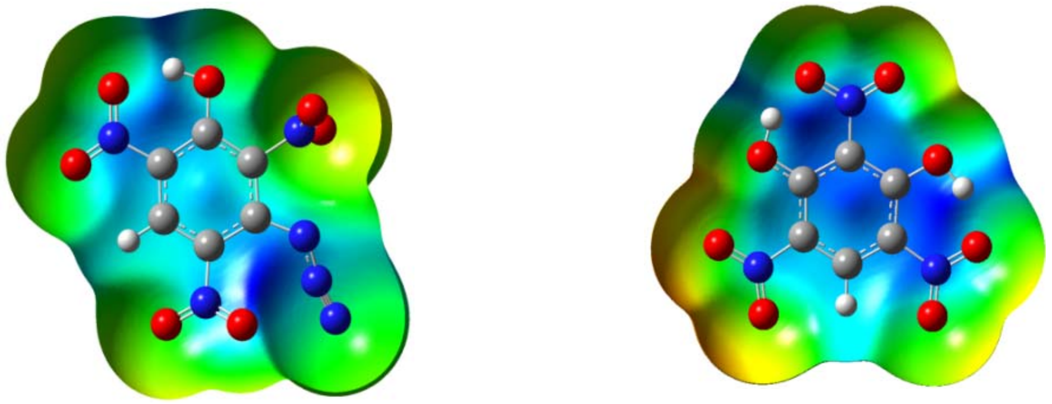
The objective of computing the molecular electrostatic potential (MESP) is to examine the insights into intermolecular association and to achieve a better understanding of the basic factors that determine the reactive properties of hydroxyl groups in these classes of high energy molecules. The MESP depends on the whole effect of all the charges in the molecule. The relative magnitudes of the positive and negative electrostatic potentials in various regions of anionic compounds are shown in Figure 5.1. The surface is taken to be the 0.001 au (electrons per Bohr^3) contour of the electronic density, as proposed by Bader et.al [21]. Regions (blue) in which the ESP is positive are electron deficient, while regions (red) which have negative potentials are electron rich. It is readily discernible that the negative potential has largely been localized near the nitro groups and strong positive potential on the H of the hydroxyl group of these compounds. This clearly represents the acidity of this proton and donation of H from the hydroxyl group to form salts with nitrogen-rich heterocyclic compounds. The introduction of –NO_2 group has the consistent effect of weakening the negative potentials associated with the C–C bonds in aromatic ring; this reflects the electron withdrawing power of the nitro group. With –OH and –CH_3 substituents, the situation is similar, however not as extreme.



Picric acid

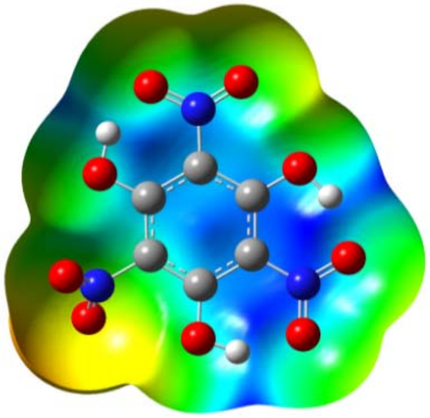


2,4,6-Trinitro-m-cresol



3-Azido-2,4,6-trinitrophenol

Styphnic acid



2,4,6-Trinitro-1,3,5-benzenetriol

Figure 5.1 *Calculated molecular electrostatic potential on the 0.001 au molecular surface of the nitrophenols. The red regions represent electron-rich regions, the blue regions extremely electron-deficient regions. Gray=carbon; white=hydrogen; blue=nitrogen; red=oxygen.*

5.3. Summary

In summary, we have synthesized and characterized different nitrophenolate salts with appropriate synthetic methods in high yields. The low cost and the availability of the starting materials, easy and clean work-up, and high yields make these salts attractive for their applications as energetic materials. Comparing energetic properties of picric acid, styphnic acid and 2,4,6-trinitro-1,3,5-benzenetriol reveals that –OH group tends to reduce heat of formation, while improving density, oxygen balance and thus, performance. All the phenolate salts exhibit good thermal stabilities, better densities, reasonable detonation pressures and detonation velocities.

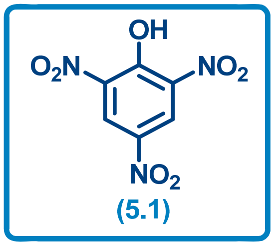
5.4. Experimental section

5.4.1. Materials and instruments

The reagents were available commercially and were used as purchased without further purification. Reactions were monitored by TLC analysis, by using precoated silica gel TLC plates obtained from Merck. ^{1}Hand ^{13}CNMRspectroscopic data were recorded on a Bruker Avance 400 MHz FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard using [D6] DMSO as the solvent. MS was performed on a LC-MS spectrometer. Melting points and decomposition temperatures were determined by DSC-TGA using TA instruments SDT Q 600 instrument. The IR spectra were recorded on a Perkin-Elmer IR spectrometer by using KBr pellets. Elemental analyses were performed on a flash EA 1112 full automatic trace element analyzer.

5.4.2. Synthetic Procedures

***Picric Acid* (*5.1*):** 2,4-Dinitrophenol (0.184 g, 0.001m) dissolved in Conc. H_2SO_4 (5 ml). Round bottom flask charged with Conc. H_2SO_4 (5 ml) and fuming nitric acid (8 ml) and cooled to approximately 5 °C. The solution of 2,4-dinitrophenol added slowly for over 30 min with stirring. After complete addition, reaction mixture stirred for additional 15 min and the cooling bath was removed. The reaction mixture subjected to heating (80 °C) for 2h. The reaction mixture was cooled and poured into crushed ice. Resulting precipitate was isolated by filtration and thoroughly washed with water to give yellow solid (0.155 g, 68%). DSC-TGA (10 °C min^{-1}): 120 °C (m.p.), 242 °C (dec).



(5.1)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3107, 3088, 1631, 1629, 1610, 1567, 1561, 1498, 1483, 1432, 1342, 1316, 1279, 1168, 1089, 938.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 10.19 (s, 1H) 8.83 (s, 2H).

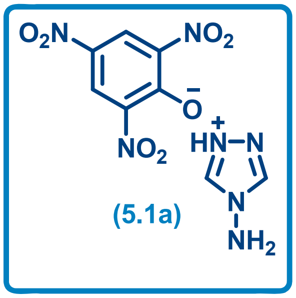
^{13}C NMR (100MHz, DMSO) : δ (ppm) 152.8, 138.8, 136.7, 125.4.

Mass : 228.

Anal. Calcd. for $C_6H_3N_3O_7$: C, 31.45; H, 1.32; N, 18.34.

Found : C, 31.34; H, 1.40; N, 18.41.

***4H-1,2,4-Triazol-4-aminium 2,4,6-trinitrophenolate* (*5.1a*):** A solution of 4-amino-4*H*-1,2,4-triazole (0.168 g, 2 mmol) was slowly added to a solution of picric acid (0.458 g, 2 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.591 g, 94% yield). DSC-TGA (10 °C min^{-1}): 192 °C (m.p.), 240 °C (dec).



(5.1a)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3364, 3254, 3112, 3079, 1621, 1567, 1539, 1484, 1419, 1364, 1326, 1265, 1156, 1084, 942.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.511 (s, 2H) 8.587 (s, 2H).

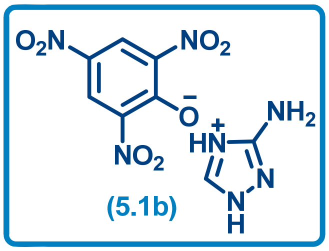
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.282, 144.469, 142.269, 125.732, 124.833.

Mass : 313.18.

Anal. Calcd. for $C_8H_7N_7O_7$: C, 30.68; H, 2.25; N, 31.31.

Found : C, 30.54; H, 2.34; N, 31.42.

***3-Amino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate* (*5.1b*):** A solution of 3-amino-1,2,4-triazole (0.168 g, 2 mmol) was slowly added to a solution of picric acid (0.458 g, 2 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.583 g, 93% yield). DSC-TGA (10 °C min^{-1}): 231 °C.


(5.1b)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3452, 3361, 3167, 3106, 1698, 1632, 1550, 1501, 1424, 1336, 1271, 1254, 1172, 1090, 953.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.601 (s, 2H) 8.329 (s, 1H).

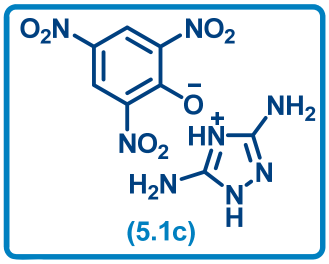
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.3, 151.1, 142.2, 139.6, 125.7, 124.7.

Mass : 313.18.

Anal. Calcd. for $C_8H_7N_7O_7$: C, 30.68; H, 2.25; N, 31.31.

Found : C, 30.55; H, 2.31; N, 31.44.

***3,5-Diamino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate* (*5.1c*):** A solution of 3,5-diamino-1,2,4-triazole (0.198 g, 2 mmol) was slowly added to a solution of picric acid (0.458 g, 2 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product.Yellow solid (0.592 g, 90% yield). DSC-TGA (10 °C min^{-1}): 241 °C (m.p.), 254 °C (dec).


(5.1c)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3468, 3424, 3315, 3172, 3265, 1693, 1660, 1616, 1534, 1495, 1474, 1336, 1380, 1265, 1167, 1084, 1002, 909.

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 8.583 (s, 2H) 7.026 (s, 4H).

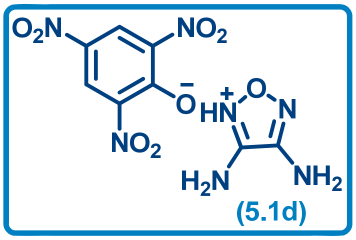
^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 161.375, 151.806, 142.220, 125.787, 124.897.

Mass : 328.20.

Anal. Calcd. for $C_8H_8N_8O_7$: C, 29.28; H, 2.46; N, 34.14.

Found : C, 29.34; H, 2.49; N, 34.28.

3,4-Diamino-1,2,5-oxadiazol-2-ium 2,4,6-trinitrophenolate **(*5.1d*):** A solution of 3,4-diaminofurazan (0.200 g, 2 mmol) was slowly added to a solution of picric acid (0.458 g, 2 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. White solid (0.625 g, 95% yield). DSC-TGA (10 °C min^{-1}): 112 °C (m.p.), 238 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) :3430, 3320, 3189, 3101, 1649, 1605, 1517, 1430, 1336, 1260, 1156, 1084, 942.

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 8.597 (s, 2H) 6.882 (s, 5H).

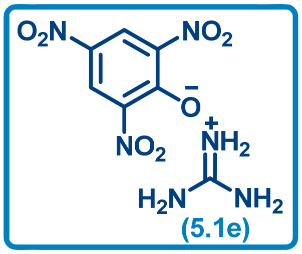
^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 160.5, 150.1, 142.0, 125.8, 125.6.

Mass : 329.18.

Anal. Calcd. for $C_8H_7N_7O_8$: C, 29.19; H, 2.14; N, 29.78.

Found : C, 29.27; H, 2.18; N, 29.64.

Diaminomethaniminium-2,4,6-trinitrophenolate **(*5.1e*):** A solution of guanidine nitrate (0.244 g, 2 mmol) was slowly added to a solution of picric acid (0.458 g, 2 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.657 g, 94% yield). DSC-TGA (10 °C min^{-1}): 120 °C (m.p.), 291 °C (dec).

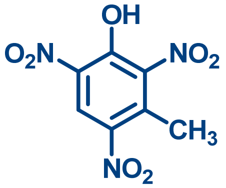


IR (KBr pellet, ν_{max}/cm^{-1}) : 3468, 3430, 3254, 3194, 3095, 1660, 1605, 1556, 1424, 1342, 1260, 1145, 1073, 915.

^{1}H NMR (400 MHz, CD_3OD) : δ (ppm) 8.591 (s, 2H), 6.944 (s, 6H).

^{13}C NMR (100MHz, CD_3OD) : δ (ppm) 161.0, 158.3, 142.0, 125.8, 125.4.
Mass : 288.17.
Anal. Calcd. for $C_7H_8N_6O_7$: C, 29.18; H, 2.80; N, 29.16.
Found : C, 29.10; H, 2.76; N, 29.09.

***2,4,6-Trinitro-m-cresol* (*5.2*):** The preparation of 2,4,6-trinitro-m-cresol is given in Scheme 5.1. A round-bottom flask was charged with sulfuric acid (98%, 20 mL) and cooled to approximately 5 °C. Potassium nitrate (0.808 g, 8 mmol) was added slowly with stirring to avoid rise in the temperature. After complete addition of potassium nitrate, reaction mixture stirred for 15 min and m-cresol (0.208 g, 2 mmol) was added at a rate such that the temperature did not exceed 10 °C. Vigorous stirring was maintained to prevent concentrating the solid in the center. After complete m-cresol addition, reaction mixture was stirred for 15 min and the cooling bath was removed. The reaction was stirred for an additional 30 min at room temperature. The reaction mixture poured into crushed ice and resulting precipitate was isolated by filtration, washed with cold 10% HCl and water. The resultant yellow solid was air dried to afford 2,4,6-trinitro-m-cresol (0.420 g, 86% yield). DSC-TGA (10 °C min^{-1}): 106 °C (m.p.), 212 °C (dec).

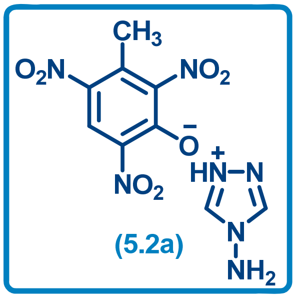


(5.2)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3326, 3210, 3106, 1643, 1594, 1545, 1463, 1424, 1342,1315, 1178, 1063, 1035, 920.
^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.739 (s, 1H) 2.340 (s, 3H).
^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.567, 149.809, 135.690, 131.132, 128.544, 126.617, 16.170.
Mass : 243.13.
Anal. Calcd. for $C_7H_5N_3O_7$: C, 34.58; H, 2.07; N, 17.28.
Found : C, 34.44; H, 2.11; N, 17.38.

***4H-1,2,4-Triazol-4-aminium 3-methyl-2,4,6-trinitrophenolate* (*5.2a*):** A solution of 4-amino-4*H*-1,2,4-triazole (0.084 g, 1 mmol), was slowly added to a solution of 2,4,6-trinitro-m-cresol

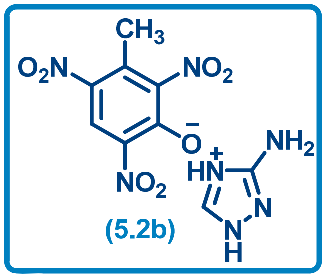
(0.243 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.307 g, 94% yield). DSC-TGA (10 °C min^{-1}): 175 °C (m.p.), 225 °C (dec).



(5.2a)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3347, 3293, 3117, 1605, 1419, 1271, 1156, 1068.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 9.494 (s, 2H) 8.740(s, 1H) 2.328 (s, 3H).
^{13}C NMR (100MHz, CD_3OD)	: δ (ppm) 160.100, 150.545, 144.478, 135.691, 130.834, 127.002, 126.905, 16.285.
Mass	: 327.21.
Anal. Calcd. for $C_9H_9N_7O_7$	: C, 33.04; H, 2.77; N, 29.96.
Found	: C, 33.18; H, 2.71; N, 29.86.

3-Amino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (***5.2b***)**:** A solution of 3-amino-1,2,4-triazole (0.084 g, 1 mmol) was slowly added to a solution of 2,4,6-trinitro-m-cresol (0.243 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.295 g, 90% yield). DSC-TGA (10 °C min^{-1}): 185 °C (m.p.), 225 °C (dec).



(5.2b)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3452, 3331, 3161, 1682, 1632, 1575, 1532, 1435, 1347, 1320, 1249, 1161, 1052, 953.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 8.722 (s, 1H) 8.300 (s, 1H) 2.312 (s, 3H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 160.259, 151.199, 150.628, 139.685, 135.725,

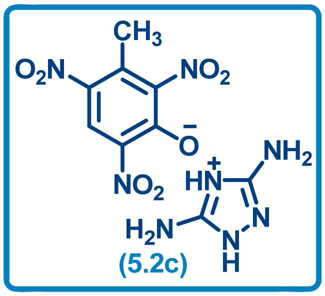
130.776, 126.919, 16.274.

Mass : 327.21.

Anal. Calcd. for $C_9H_9N_7O_7$: C, 33.04; H, 2.77; N, 29.96.

Found : C, 33.11; H, 2.69; N, 29.89.

3,5-Diamino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate **(*5.2c*):** A solution of 3,5-diamino-1,2,4-triazole (0.099 g, 1 mmol) was slowly added to a solution of 2,4,6-trinitro-m-cresol (0.243 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.319 g, 93% yield). DSC-TGA (10 °C min^{-1}): 206 °C (m.p.), 235 °C (dec).



(5.2c)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3463, 3369, 3189, 1698, 1660, 1627, 1567, 1528, 1309, 1249, 1150, 1079, 1024, 920.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.744 (s, 1H) 2.334 (s, 3H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 160.289, 151.886, 150.610, 135.690, 130.823, 126.925, 126.883, 16.268.

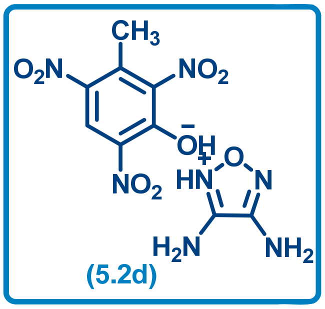
DEPT NMR (100MHz, DMSO) : δ (ppm) 126.998, 16.268.

Mass : 342.23.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.59; H, 2.95; N, 32.74.

Found : C, 31.51; H, 2.87; N, 32.68.

3,4-Diamino-1,2,5-oxadiazol-2-ium 3-methyl-2,4,6-trinitrophenolate **(*5.2d*):** A solution of 3,4-diaminofurazan (0.100 g, 1 mmol) was slowly added to a solution of 2,4,6-trinitro-m-cresol (0.243 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Brown solid (0.302 g, 88% yield). DSC-TGA (10 °C min^{-1}): 103 °C (m.p.), 211 °C (dec).



(5.2d)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3424, 3320, 3260, 3106, 1638, 1594, 1545, 1452, 1353, 1315, 1161, 1068, 920.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.745 (s, 1H) 7.200(s, 4H) 2.346 (s, 3H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.659, 150.172, 149.851, 135.712, 131.142, 128.539, 126.594, 16.171.

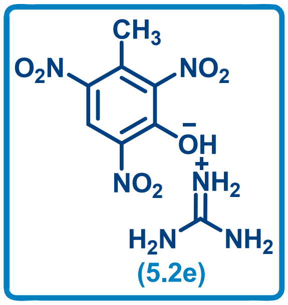
DEPT NMR (100MHz, DMSO) : δ (ppm) 126.598, 16.174.

Mass : 343.21.

Anal. Calcd. for $C_9H_9N_7O_8$: C, 33.04; H, 2.77; N, 29.96.

Found : C, 33.11; H, 2.69; N, 29.89.

Diaminomethaniminium 3-methyl-2,4,6-trinitrophenolate **(*5.2e*):** A solution of guanidine nitrate (0.122 g, 1 mmol) was slowly added to a solution of 2,4,6-trinitro-m-cresol (0.243 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.338 g, 93% yield). DSC-TGA (10 °C min^{-1}): 107 °C (m.p.), 175 °C (dec).



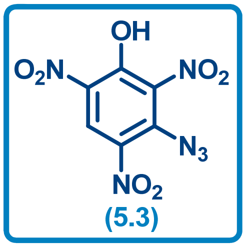
(5.2e)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3408, 3205, 3106, 1665, 1638, 1594, 1539, 1463, 1419, 1347, 1172, 1063, 915.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.738 (s, 1H) 6.948(s, 6H) 2.336 (s, 3H).

^{13}C NMR (100MHz, DMSO)	: δ (ppm) 158.849, 158.381, 149.882, 135.652, 131.183, 128.529, 126.613, 16.151.
DEPT NMR (100MHz, DMSO)	: δ (ppm) 126.617, 16.154.
Mass	: 302.20.
Anal. Calcd. for $C_8H_{10}N_6O_7$	: C, 31.80; H, 3.34; N, 27.81.
Found	: C, 31.70; H, 3.17; N, 27.76.

3-Azido-2,4,6-trinitrophenol (***5.3***)**:** The preparation of 3-azido-2,4,6-trinitrophenol is given in Scheme 5.2. To a 100 ml round-bottomed flask, 10 ml of concentrated H_2SO_4 was transferred and 8 ml of fuming nitric acid was added drop wise at room temperature with stirring. After complete addition, nitrating mixture chilled to approximately 5 °C. To this nitrating mixture, 3-chlorophenol (0.645 g, 5 mmol) was added slowly over a period of 30 min to avoid vigorous reaction. After complete addition, ice bath removed and reaction mixture subjected to heating (70 °C) for 2h. The reaction mixture was cooled and poured into crushed ice. Resulting precipitate was isolated by filtration and thoroughly washed with water to give 3-chloro-2,4,6-trinitrophenol yellow solid (0.920 g, 75%). This compound (0.396 g, 1.5 mmol) dissolved in methanol (10 mL) and sodium azide (0.117 g, 1.8 mmol) was added and the reaction continued for 2h at room temperature. The resulting mixture was heated at reflux for an additional 2h. After this, the solvent was removed and the residue was extracted with ethyl acetate and washed with water. The solvent was removed under reduced pressure to give pure product **3** (0.380 g, 94% yield). DSC-TGA (10 °C min^{-1}): 86 °C (m.p.), 254 °C (dec).

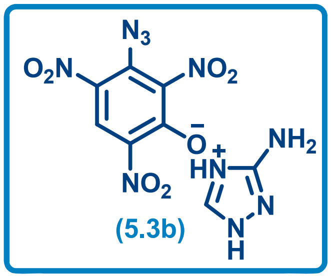


(5.3)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3495, 2920, 2849, 2136, 1660, 1578, 1528, 1484, 1347, 1260, 1117.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 8.76 (s, 1H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 159.4, 149.1, 136.5, 127.3, 124.3.

DEPT NMR (100MHz, DMSO) : δ (ppm) 127.3.
Mass : 270.12.
Anal. Calcd. for $C_6H_2N_6O_7$: C, 26.68; H, 0.75; N, 31.11.
Found : C, 26.54; H, 0.72; N, 31.02.

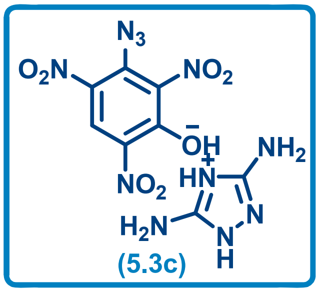
3-Amino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (***5.3b***)**:** A solution of 3-amino-1,2,4-triazole (0.084 g, 1 mmol) was slowly added to a solution of 3-azido-2,4,6-trinitrophenol (0.270 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Brown solid (0.295 g, 83% yield). DSC-TGA (10 °C min^{-1}): 119 °C (m.p.), 191 °C (dec).



(5.3b)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3048, 2164, 2054. 1660, 1578, 1550, 1534, 1501, 1457, 1353, 1260, 1123, 1057, 997, 750.
^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.054 (s, 1H) 7.405 (s, 1H) 5.833 (s, 2H).
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.7, 157.2, 149.4, 148.3, 135.2, 127.5, 115.2, 111.4.
Mass : 354.20.
Anal. Calcd. for $C_8H_6N_{10}O_7$: C, 27.13; H, 1.71; N, 39.54.
Found : C, 27.01; H, 1.74; N, 39.47.

3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (***5.3c***)***:*** A solution of 3,5-diamino-1,2,4-triazole (0.099 g, 1 mmol) was slowly added to a solution of 3-azido-2,4,6-trinitrophenol (0.270 g, 01 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Brown solid (0.319 g, 86% yield). DSC-TGA (10 °C min^{-1}): 210 °C.



(5.3c)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3408, 2920, 2153, 2049, 1649, 1567, 1490, 1408, 1375, 1347, 1254, 1128, 1063.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.033 (s, 1H) 5.168 (s, 4H).

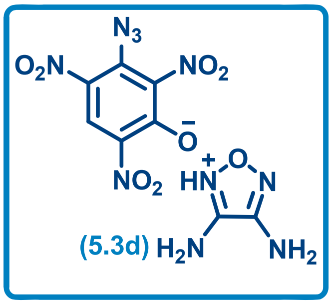
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.7, 148.3, 135.2, 127.5, 115.2, 111.4.

Mass : 369.21.

Anal. Calcd. for $C_8H_7N_{11}O_7$: C, 26.02; H, 1.91; N, 41.73.

Found : C, 25.84; H, 1.98; N, 41.85.

***3,4-Diamino-1,2,5-oxadiazol-2-ium 3-azido-2,4,6-trinitrophenolate* (*5.3d*):** A solution of 3,4-diaminofurazan (0.100 g, 1 mmol) was slowly added to a solution of 3-azido-2,4,6-trinitrophenol (0.270 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Brown solid (0.302 g, 82% yield). DSC-TGA (10 °C min^{-1}): 78 °C (m.p.), 198 °C (dec).



(5.3d)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3441, 3309, 3260, 2926, 2147, 2054, 1649, 1572, 1528, 1473, 1347, 1260, 1128, 1002, 975.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.051 (s, 1H) 5.931 (s, 4H).

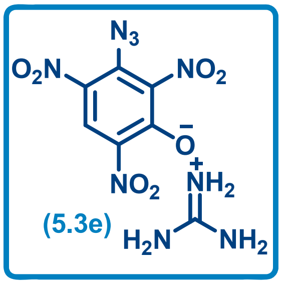
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.7, 150.2, 148.3, 135.2, 127.5, 115.1, 111.4.

Mass : 370.20.

Anal. Calcd. for $C_8H_6N_{10}O_8$: C, 25.96; H, 1.63; N, 37.84.

Found : C, 25.79; H, 1.74; N, 37.96.

Diaminomethaniminium 3-azido-2,4,6-trinitrophenolate (***5.3e***)**:** guanidine nitrate (0.122 g, 1 mmol) was slowly added to a solution of 3-azido-2,4,6-trinitrophenol (0.270 g, 1 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.338g, 86% yield). DSC-TGA (10 °C min^{-1}): 156 °C (dec).


(5.3e)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3589, 3402, 2147, 2049, 1650, 1567, 1528, 1479, 1347, 1123, 986.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.056 (s, 1H) 7.063 (s, 6H).

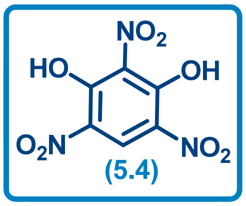
^{13}C NMR (100MHz, DMSO) : δ (ppm) 161.7, 158.5, 148.3, 135.2, 127.5, 115.2, 111.4.

Mass : 329.19.

Anal. Calcd. for $C_7H_7N_9O_7$: C, 25.54; H, 2.14; N, 38.29.

Found : C, 25.41; H, 2.10; N, 38.20.

Styphnic acid (***5.4***)**:** The preparation of styphnic acid is given in Scheme 5.3. The compound was prepared from two different starting materials, 2-nitroresorcinol (0.620 g, 4 mmol) and resorcinol (0.550 g, 0.5 mmol) with the similar method for compound **5.2**, forming a yellow solid in 88% yield. DSC-TGA (10 °C min^{-1}): 173°C (m.p.), 190 °C (dec).


(5.4)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3649, 3577, 3177, 1648, 1582, 1544, 1467, 1374, 1308, 1166, 1073, 919.

^1H NMR (400 MHz, DMSO) : δ (ppm) 8.608 (s, 1H) 6.744(s, 2H).

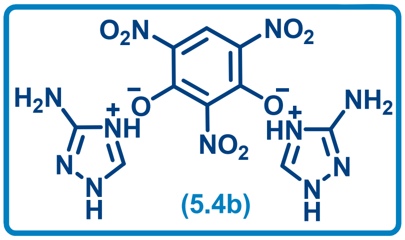
^{13}C NMR (100MHz, DMSO) : δ (ppm) 155.7, 135.4, 126.1, 126.0.

Mass : 245.10.

Anal. Calcd. for $C_6H_3N_3O_8$: C, 29.40; H, 1.23; N, 17.14.

Found : C, 29.54; H, 1.12; N, 17.03.

***Bis(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate* (*5.4b*): :** A solution of 3-amino-1,2,4-triazole (0.084 g, 1 mmol) was slowly added to a solution of styphnic acid (0.123 g, 0.5 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.184 g, 89% yield). DSC-TGA (10 °C min^{-1}): 227 °C (dec).


(5.4b)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3304, 3139, 1698, 1600, 1556, 1490, 1304, 1189, 1079, 958.

^1H NMR (400 MHz, DMSO) : δ (ppm) 8.628 (s, 1H) 7.883 (s, 1H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.3, 154.7, 143.9, 135.6, 126.2, 125.8.

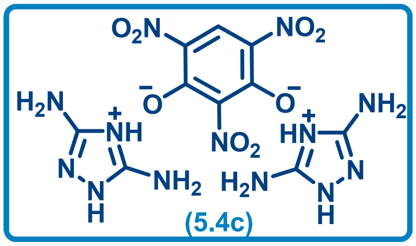
DEPT NMR (100MHz, DMSO) : δ (ppm) 143.9, 126.6.

Mass : 413.26.

Anal. Calcd. for $C_{10}H_{11}N_{11}O_8$: C, 29.06; H, 2.68; N, 37.28.

Found : C, 29.17; H, 2.61; N, 37.12.

***Bis(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate* (*5.4c*):** A solution of 3,5-diamino-1,2,4-triazole (0.099 g, 1 mmol) was slowly added to a solution of styphnic acid (0.123 g, 0.5 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.184 g, 89% yield). DSC-TGA (10 °C min^{-1}): 248 °C (dec).



(5.4c)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3451, 3407, 3270, 3183, 1703, 1648, 1572, 1478, 1385, 1308, 1199, 1045, 1002, 936.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.66 (s, 1H) 7.25 (s, 8H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.0, 154.5, 136.3, 126.9, 126.1.

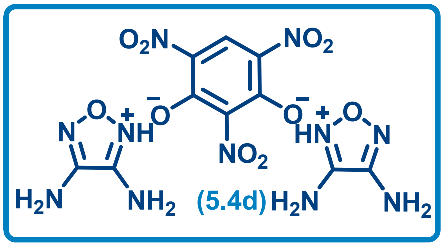
DEPT NMR (100MHz, DMSO) : δ (ppm) 126.9.

Mass : 443.29.

Anal. Calcd. for $C_{10}H_{13}N_{13}O_8$: C, 27.09; H, 2.96; N, 41.08.

Found : C, 27.17; H, 2.93; N, 40.95.

***Bis(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3-diolate* (*5.4d*):):** A solution of 3,4-diaminofurazan (0.100 g, 1 mmol) was slowly added to a solution of styphnic acid (0.123 g, 0.5 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.21 g, 95% yield). DSC-TGA (10 °C min^{-1}): 146 °C (m.p.), 219 °C (dec).



(5.4d)

IR (KBr pellet, ν_{max}/cm^{-1}) : 2915, 2849, 2706, 2597, 2010, 1747, 1594, 1528, 1473, 1331, 1249, 1210, 1123, 1057, 1008, 920.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.63 (s, 1H) 6.25 (s, 8H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 155.9, 150.1, 135.4, 126.1, 125.9.

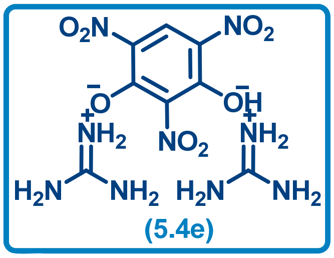
DEPT NMR (100MHz, DMSO) : δ (ppm) 126.1.

Mass : 445.26.

Anal. Calcd. for $C_{10}H_{11}N_{11}O_{10}$: C, 26.97; H, 2.49; N, 34.60.

Found : C, 26.87; H, 2.54; N, 34.50.

Bis(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3-diolate (***5.4e***)**:** A solution of guanidine nitrate (0.122 g, 1 mmol) was slowly added to a solution of styphnic acid (0.123 g, 0.5 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Gray solid (0.234 g, 95% yield). DSC-TGA (10 °C min^{-1}): 199 °C (dec).



(5.4e)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3643, 3413, 3331, 3199, 1665, 1577, 1539, 1467, 1363, 1308, 1160, 1067, 919.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.63 (s, 1H) 6.96 (s, 12H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.3, 156.0, 135.4, 126.2, 125.8.

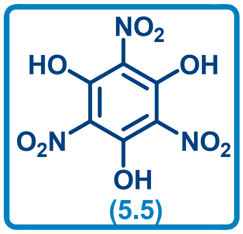
DEPT NMR (100MHz, DMSO) : δ (ppm) 126.2.

Mass : 363.24.

Anal. Calcd. for $C_8H_{13}N_9O_8$: C, 26.45; H, 3.61; N, 34.70.

Found : C, 26.56; H, 3.55; N, 34.78.

2,4,6-Trinitro-1,3,5-benzenetriol (***5.5***)**:** The preparation of 2,4,6-trinitro-1,3,5-benzenetriol is given in Scheme 5.4. The compound was prepared from two different starting materials, 2-nitrophloroglucinol (0.684 g, 4 mmol) and phloroglucinol (0.630 g, 5 mmol) with the similar method for compound **5.2**, forming a yellow solid in 90% yield. DSC-TGA (10 °C min^{-1}): 166 °C (m.p.), 191 °C (dec).



(5.5)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3643, 3577, 1637, 1582, 1528, 1413, 1352, 1308, 1210, 1171, 1111, 908.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 6.633 (s, 3H).

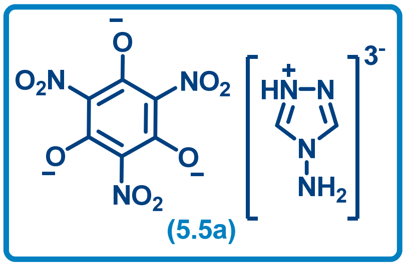
^{13}C NMR (100MHz, DMSO) : δ (ppm) 154.2, 122.4.

Mass : 261.10.

Anal. Calcd. for $C_6H_3N_3O_9$: C, 27.60; H, 1.16; N, 16.09.

Found : C, 27.68; H, 1.12; N, 15.96.

Tris(4H-1,2,4-triazol-4-aminium) 2,4,6-trinitrobenzene-1,3,5-triolate **(*5.5a*):** A solution of 4-amino-4*H*-1,2,4-triazole (0.101 g, 1.2 mmol) was slowly added to a solution of 2,4,6-trinitro-1,3,5-benzenetriol (0.104 g, 0.4 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.185g, 90% yield). DSC-TGA (10 °C min^{-1}): 196 °C (dec).



(5.5a)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3429, 3287, 3122, 1615, 1506, 1374, 1254, 1193, 1067, 1023, 892.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.71 (s, 6H), 6.07 (s, 9H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 154.6, 144.5, 122.3.

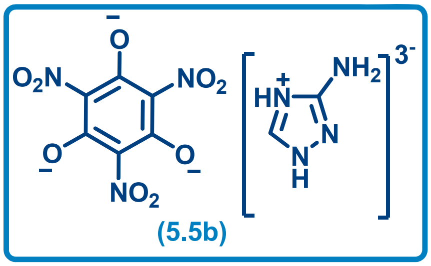
DEPT NMR (100MHz, DMSO) : δ (ppm) 143.9, 126.6.

Mass : 513.34.

Anal. Calcd. for $C_{12}H_{15}N_{15}O_9$: C, 28.08; H, 2.95; N, 40.93.

Found : C, 28.21; H, 3.05; N, 40.99.

***Tris(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate* (*5.5b*):** A solution of 3-amino-1,2,4-triazole (0.101 g, 1.2 mmol) was slowly added to a solution of 2,4,6-trinitro-1,3,5-benzenetriol (0.104 g, 0.4 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.176 g, 86% yield). DSC-TGA (10 °C min^{-1}): 147 °C (m.p.), 223 °C (dec).



(5.5b)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3419, 3315, 3150, 3052, 1687, 1638, 1556, 1490, 1331, 1238, 1123, 1041, 944.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 7.724 (s, 3H).

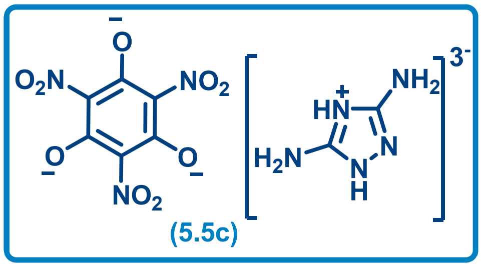
^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.1, 155.9, 145.5, 122.6.

Mass : 513.34.

Anal. Calcd. for $C_{12}H_{15}N_{15}O_9$: C, 28.08; H, 2.95; N, 40.93.

Found : C, 28.01; H, 3.07; N, 41.05.

***Tris(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate* (*5.5c*):** A solution of 3,5-diamino-1,2,4-triazole (0.119 g, 1.2 mmol) was slowly added to a solution of 2,4,6-trinitro-1,3,5-benzenetriol (0.104 g, 0.4 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Orange solid (0.198 g, 89% yield). DSC-TGA (10 °C min^{-1}): 202 °C (dec).



(5.5c)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3446, 3402, 3309, 3188, 3122, 1703, 1654, 1621, 1572, 1489, 1413, 1368, 1254, 1056, 1002.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 7.493 (s, 12H).

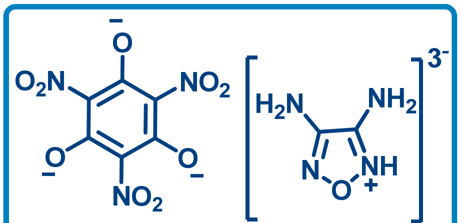
^{13}C NMR (100MHz, DMSO) : δ (ppm) 159.4, 155.5, 123.6.

Mass : 558.39.

Anal. Calcd. for $C_{12}H_{18}N_{18}O_9$: C, 25.81; H, 3.25; N, 45.15.

Found : C, 25.96; H, 3.30; N, 45.02.

***Tris(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3,5-triolate* (*5.5d*):** A solution of 3,4-diaminofurazan (0.120 g, 1.2 mmol) was slowly added to a solution of 2,4,6-trinitro-1,3,5-benzenetriol (0.104 g, 0.4 mmol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.202 g, 90% yield). DSC-TGA (10 °C min^{-1}): 182 °C (dec).



(5.5d)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3616, 3528, 3424, 3320, 3254, 3265, 3117, 1632, 1182, 1511, 1478, 1347, 1193, 1171, 969.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 6.422 (s, 12H).

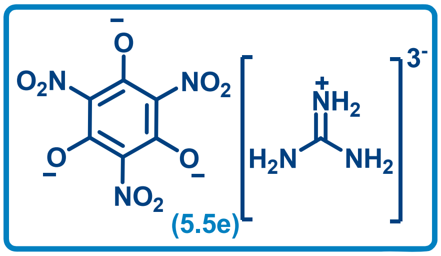
^{13}C NMR (100MHz, DMSO) : δ (ppm) 154.3, 150.1, 122.4.

Mass : 561.34.

Anal. Calcd. for $C_{12}H_{15}N_{15}O_{12}$: C, 25.68; H, 2.69; N, 37.43.

Found : C, 25.81; H, 2.74; N, 37.34.

Tris(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3,5-triolate **(*5.5e*):** A solution of guanidine nitrate (0.146 g, 0.0012m) was slowly added to a solution of 2,4,6-trinitro-1,3,5-benzenetriol (0.104 g, 0.0004mol) in methanol (12 mL) at 25 °C with stirring. After stirring for 6 h at room temperature, the solvent was removed in vacuo to leave the desired product. Yellow solid (0.223 g, 89% yield). DSC-TGA (10 °C min^{-1}): 170 °C (dec).



(5.5e)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3435, 3336, 3259, 3199, 1522, 1462, 1369, 1314, 1193, 1139, 903.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 6.98 (s, 18H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.3, 154.5, 122.3.

Mass : 438.81.

Anal. Calcd. for $C_9H_{18}N_{12}O_9$: C, 24.66; H, 4.14; N, 38.35.

Found : C, 24.78; H, 4.10; N, 38.48.

5.5. References

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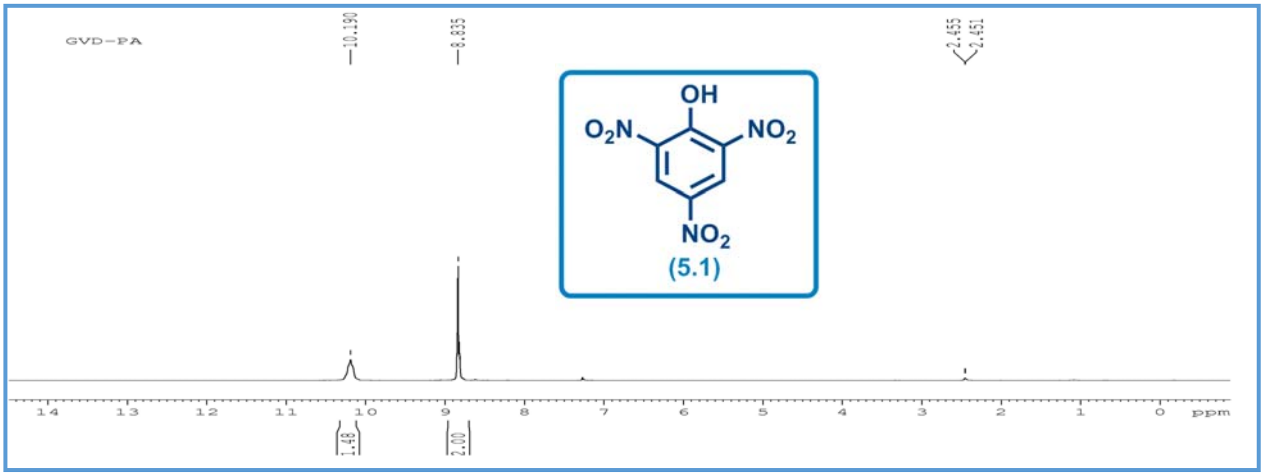


Figure 6.S1 *^{1}H NMR spectrum of Picric acid* ***(5.1)***.

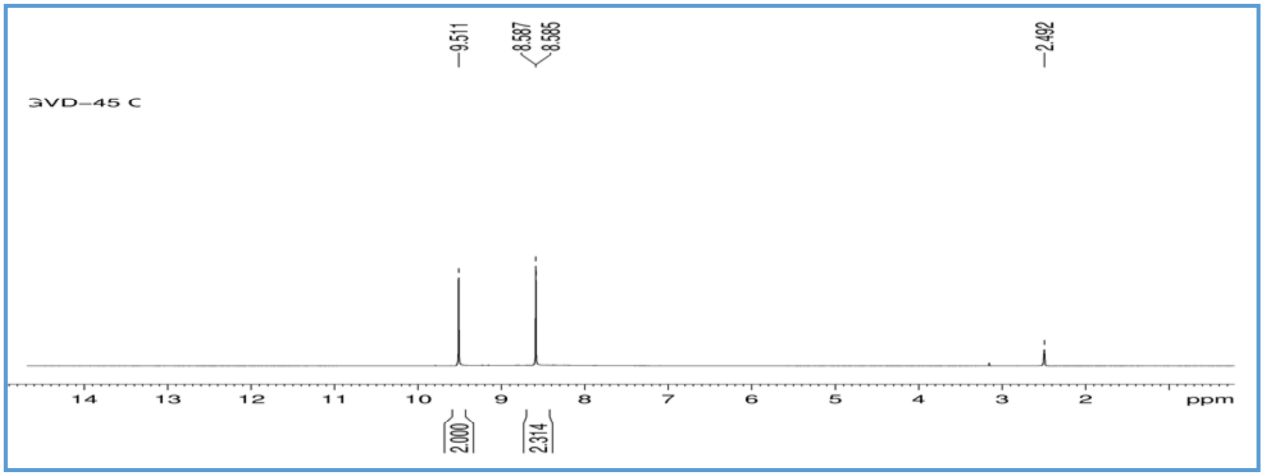


Figure 6.S2 *^{13}C NMR spectrum of Picric acid* ***(5.1)***.

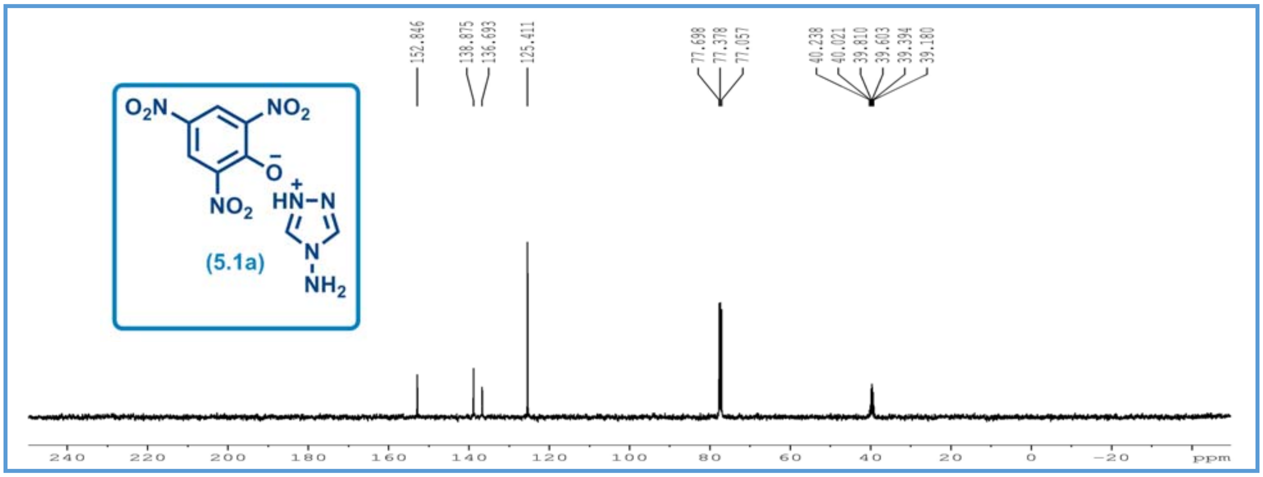


Figure 6.S3 *^{1}H NMR spectrum of 4H-1,2,4-Triazol-4-aminium 2,4,6-trinitrophenolate (**5.1a**)*

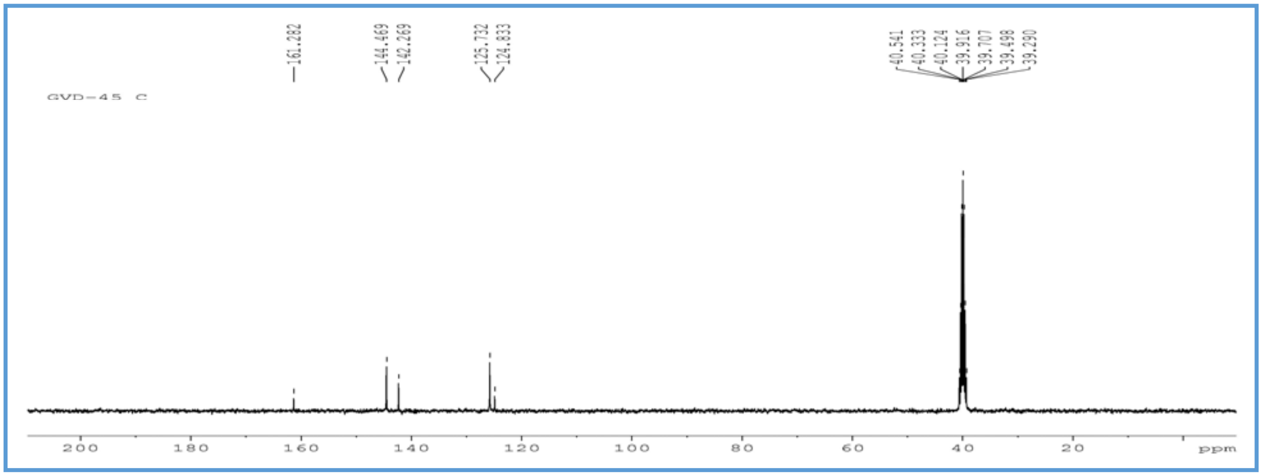


Figure 6.S4 *^{13}C NMR spectrum of 4H-1,2,4-Triazol-4-aminium 2,4,6-trinitrophenolate (**5.1a**)*

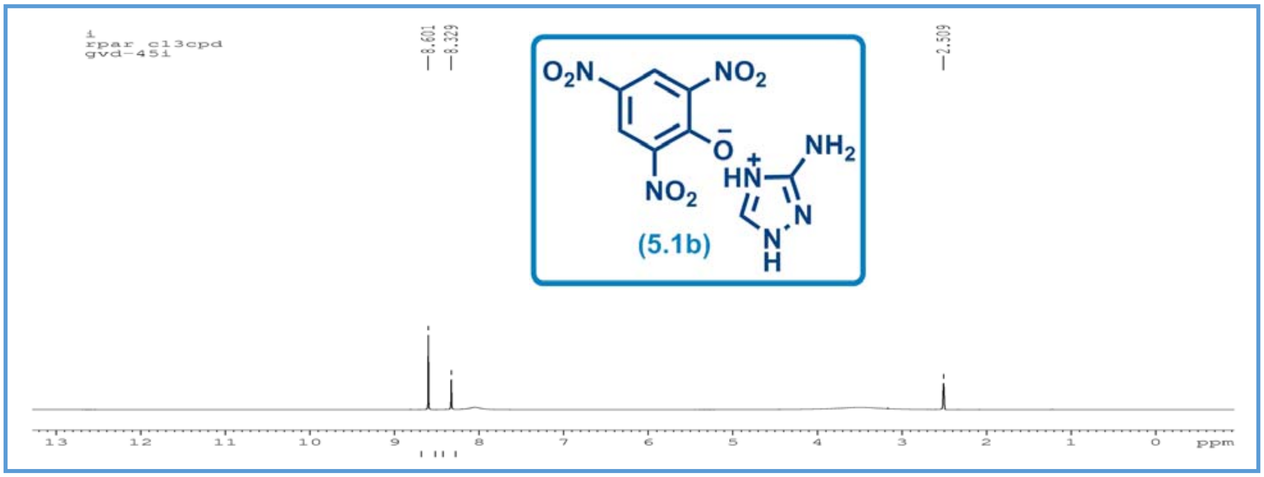


Figure 6.S5 *^{1}H NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate (**5.1b**)*

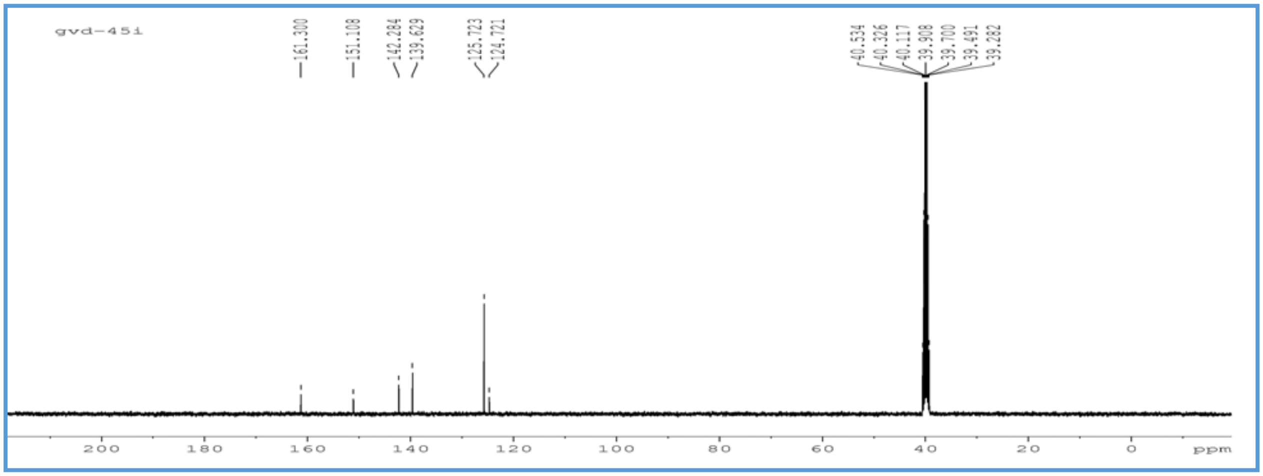


Figure 6.S6 *^{13}C NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate (**5.1b**)*

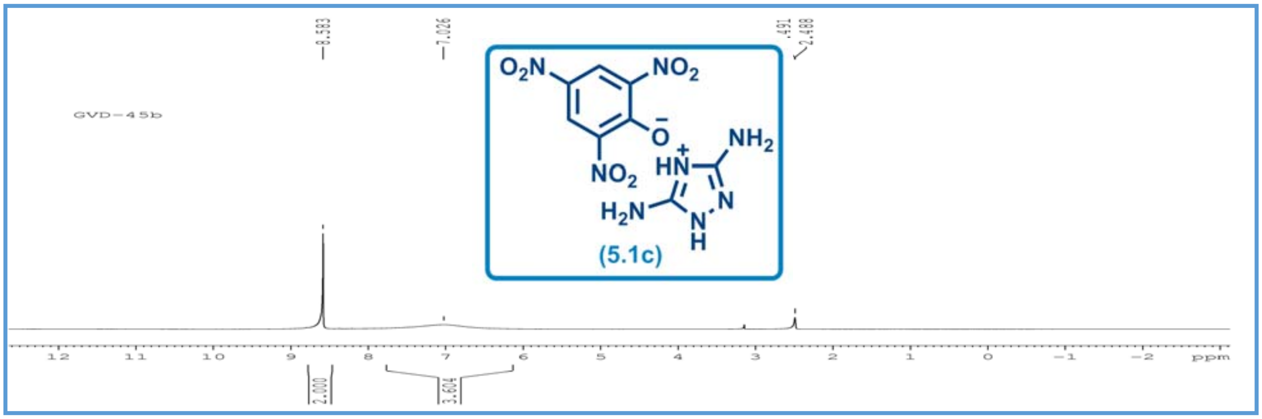


Figure 6.S7 ^{1}H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate (**5.1c**)

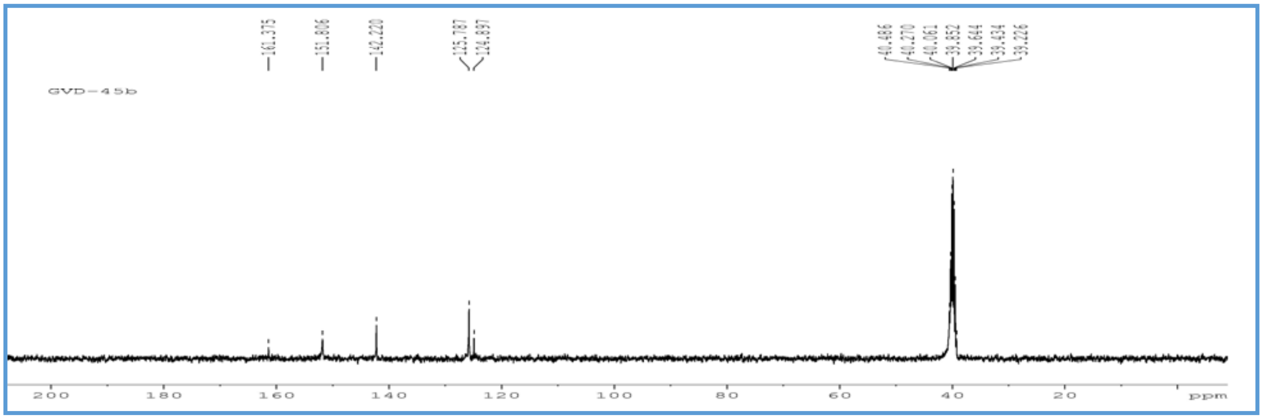


Figure 6.S8 ^{13}C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium-2,4,6-trinitrophenolate (**5.1c**)

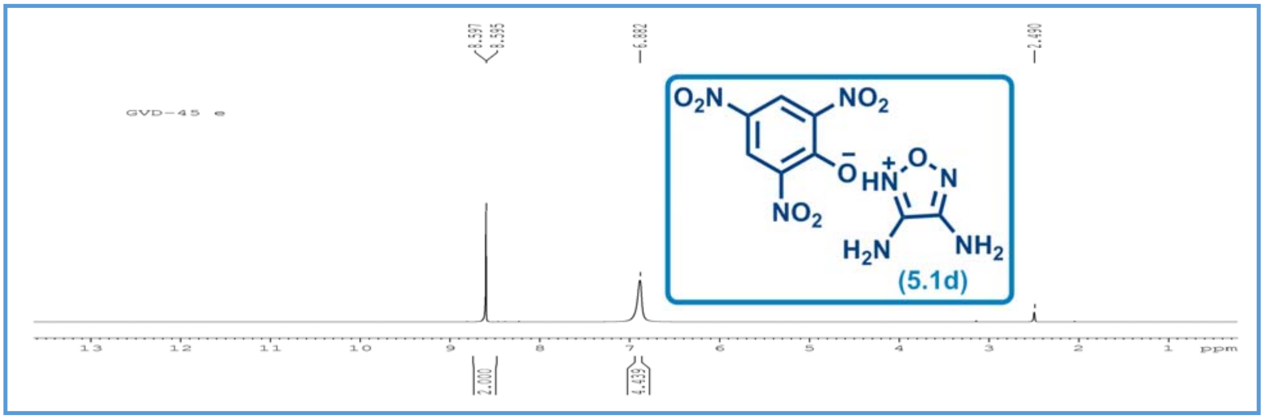


Figure 6.S9 ^{1}H NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 2,4,6-trinitrophenolate (**5.1d**)

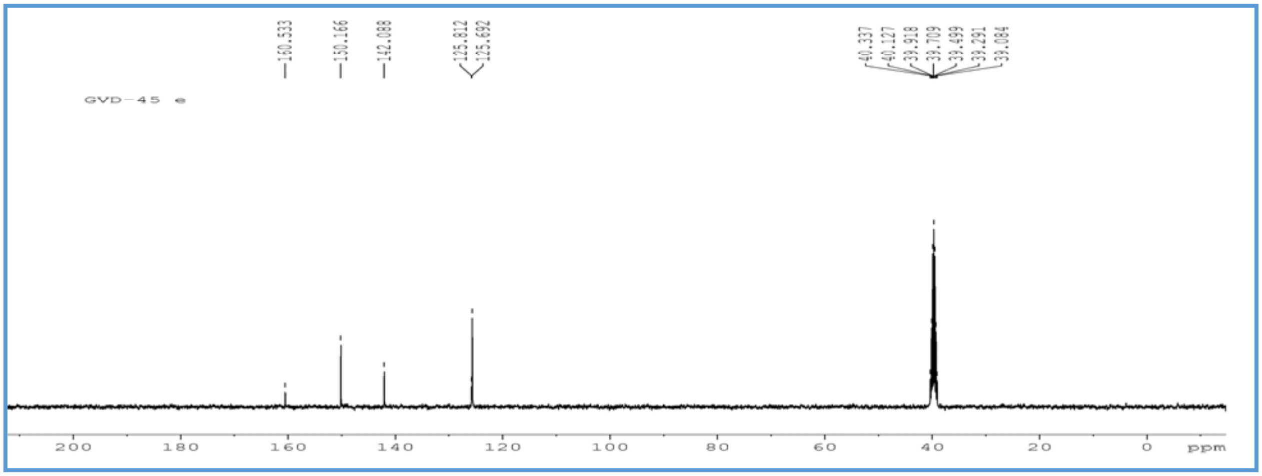


Figure 6.S10 *^{13}C NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 2,4,6-trinitrophenolate (**5.1d**)*

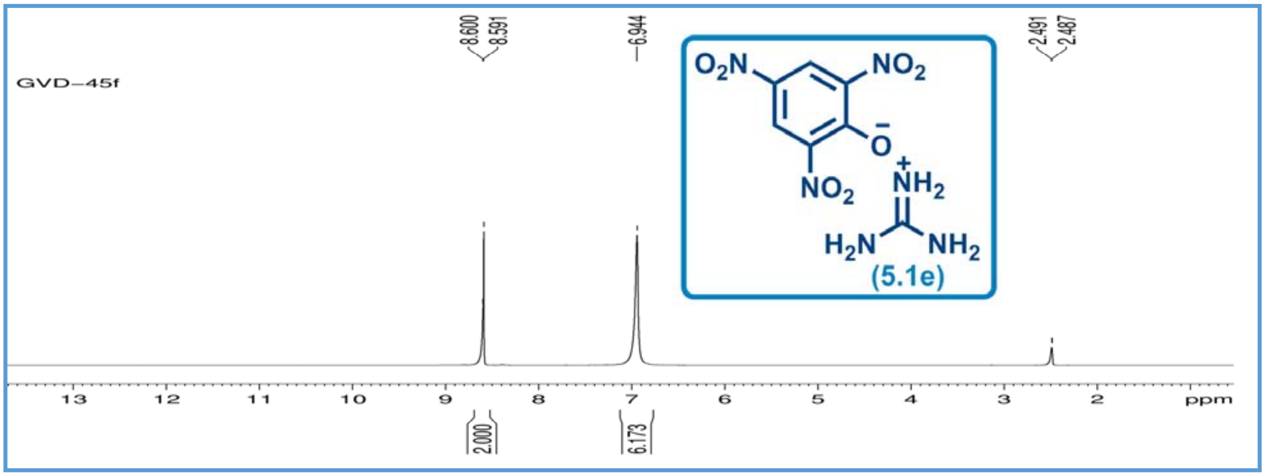


Figure 6.S11 *^{1}H NMR spectrum of Diaminomethaniminium-2,4,6-trinitrophenolate (**5.1e**)*

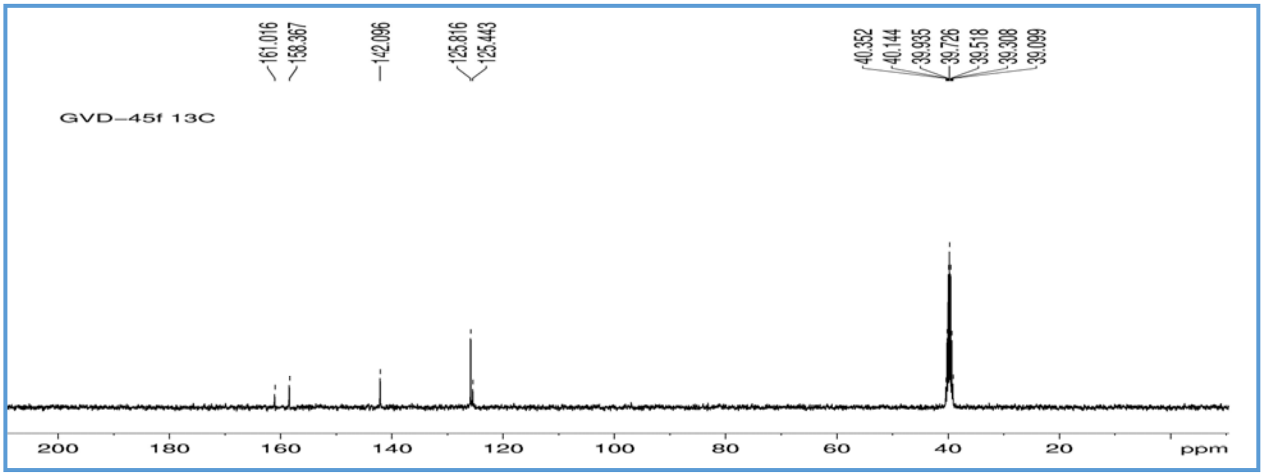


Figure 6.S12 *^{13}C NMR spectrum of Diaminomethaniminium-2,4,6-trinitrophenolate (**5.1e**)*

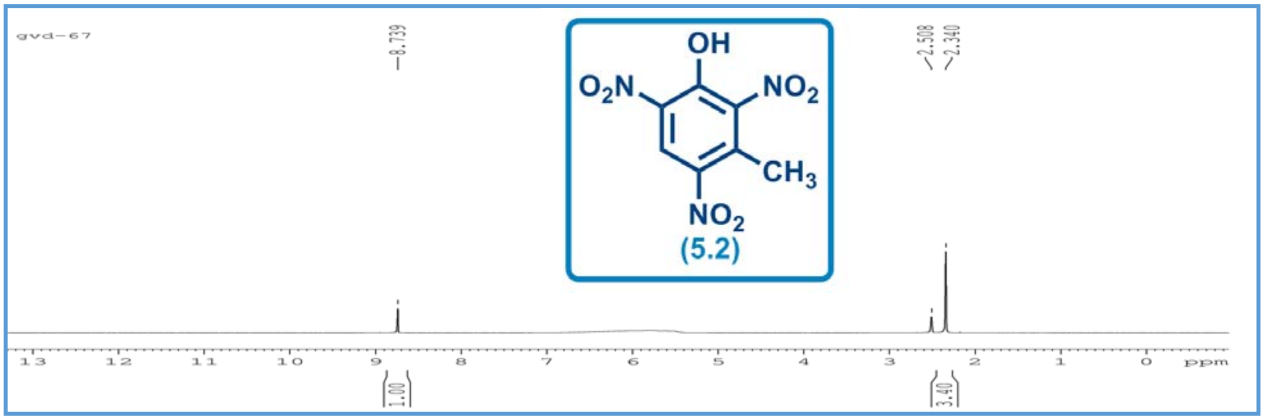


Figure 6.S13 *^{1}H NMR spectrum of 2,4,6-Trinitro-m-cresol (**5.2**)*

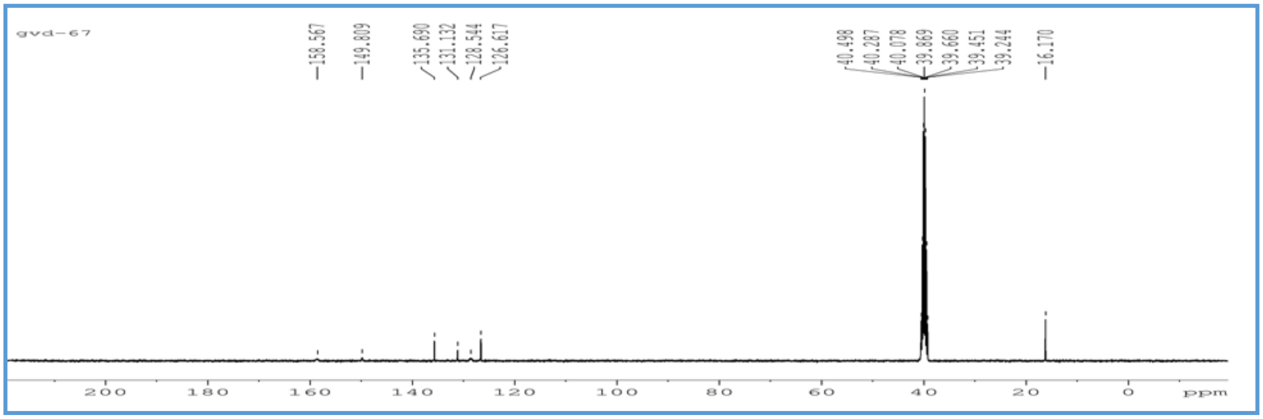


Figure 6.S14 *^{13}C NMR spectrum of 2,4,6-Trinitro-m-cresol (**5.2**)*

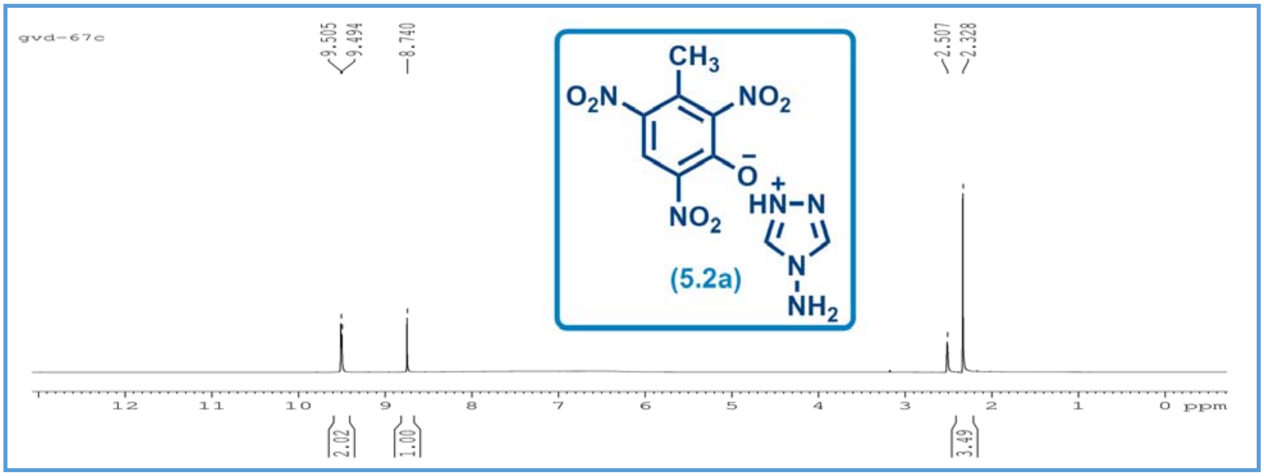


Figure 6.S15 *^{1}H NMR spectrum of 4H-1,2,4-Triazol-4-aminium 3-methyl-2,4,6-trinitrophenolate (**5.2a**)*

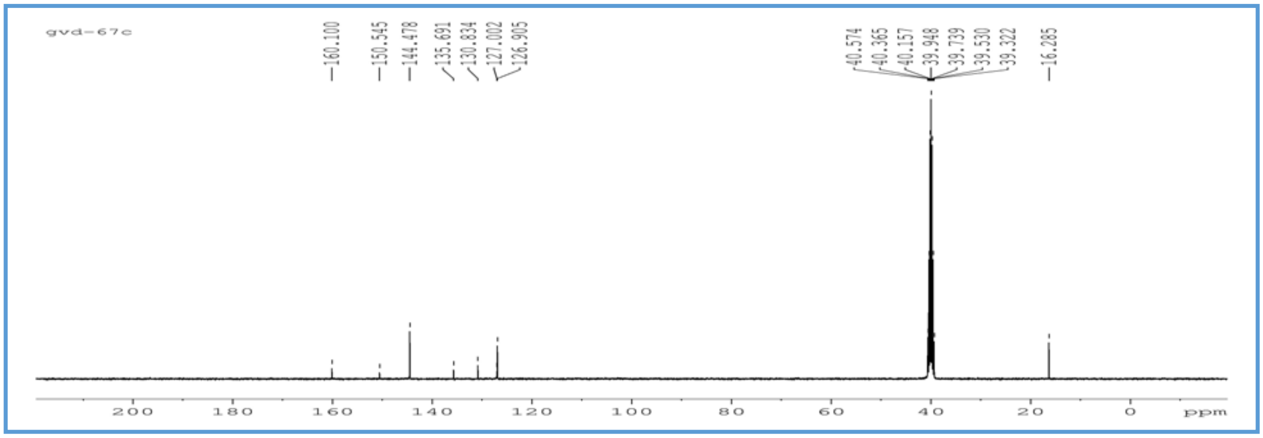


Figure 6.S16 *^{13}C NMR spectrum of 4H-1,2,4-Triazol-4-aminium 3-methyl-2,4,6-trinitrophenolate (**5.2a**)*

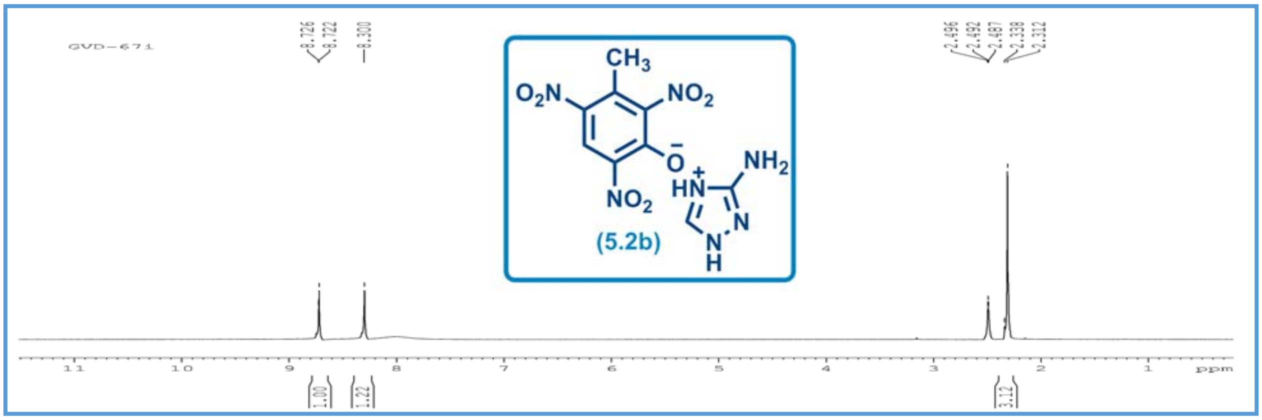


Figure 6.S17 *^{1}H NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (**5.2b**)*

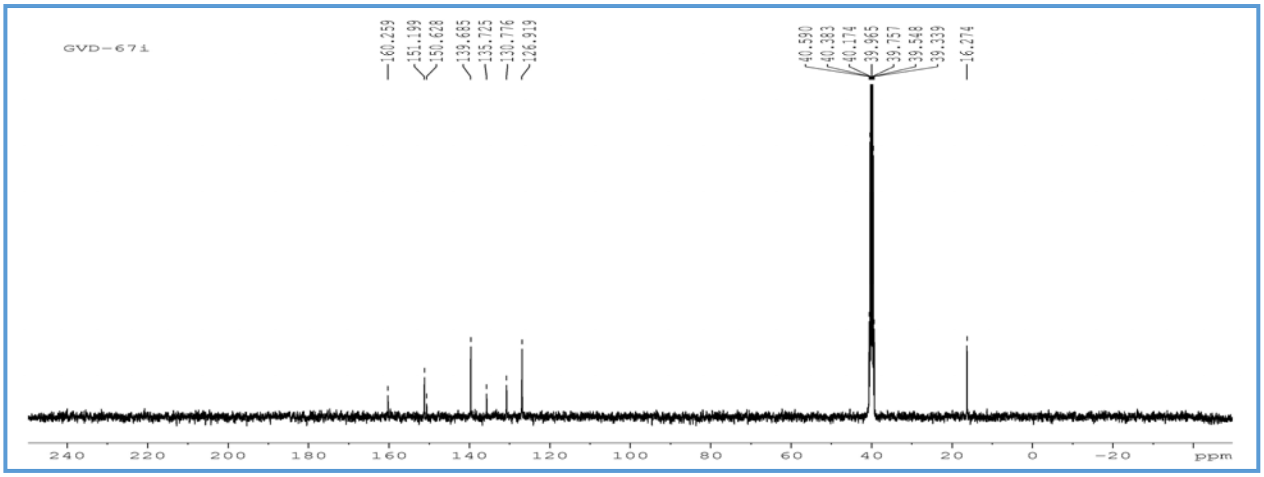


Figure 6.S18 *^{13}C NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (**5.2b**)*

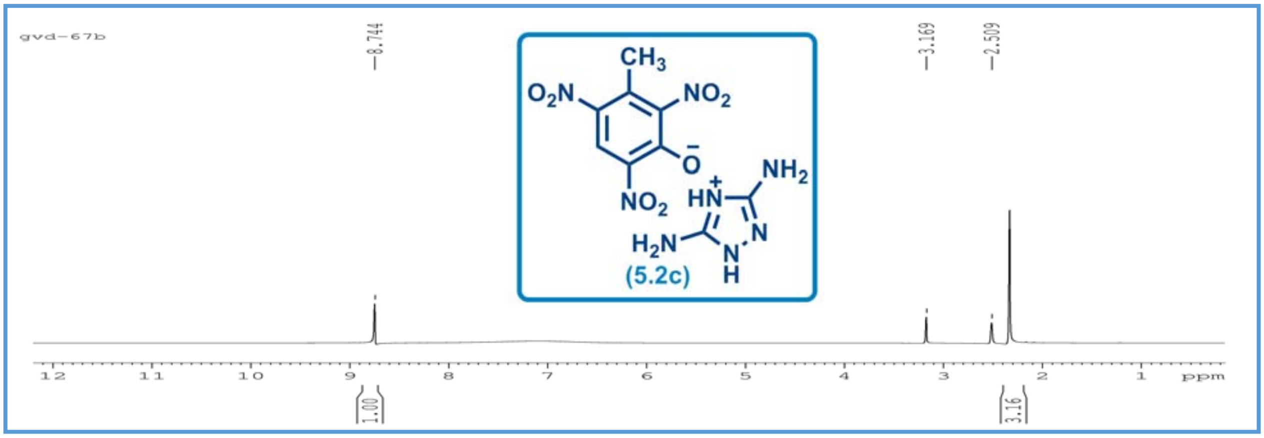


Figure 6.S19 ^{1}H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (**5.2c**)

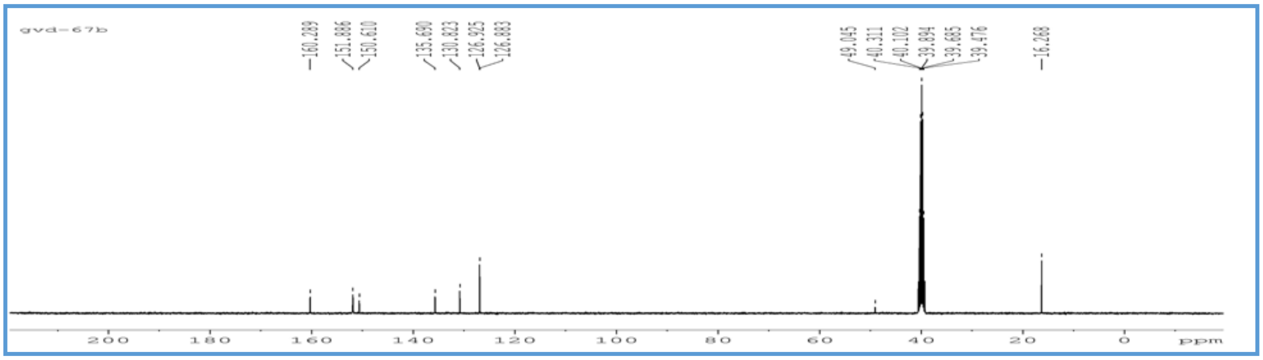


Figure 6.S20 ^{13}C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-methyl-2,4,6-trinitrophenolate (**5.2c**)

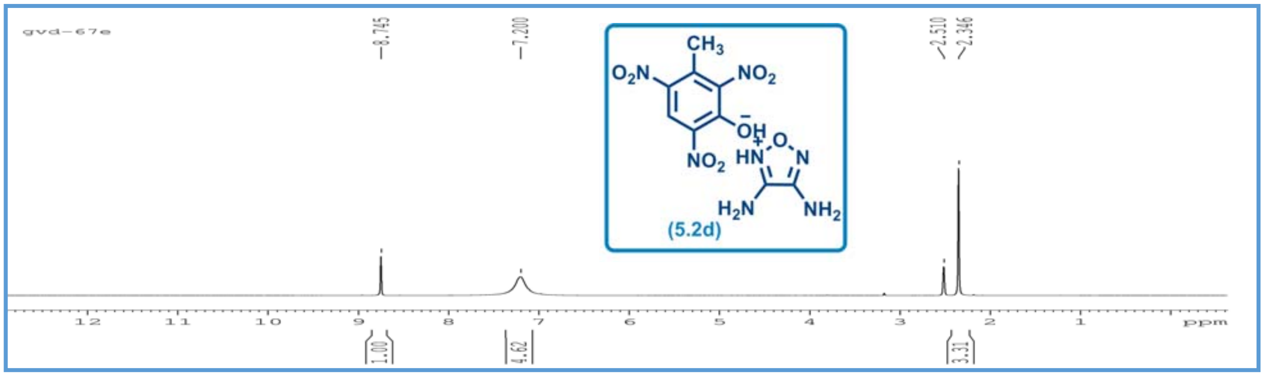


Figure 6.S21 ^{1}H NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 3-methyl-2,4,6-trinitrophenolate (**5.2d**)

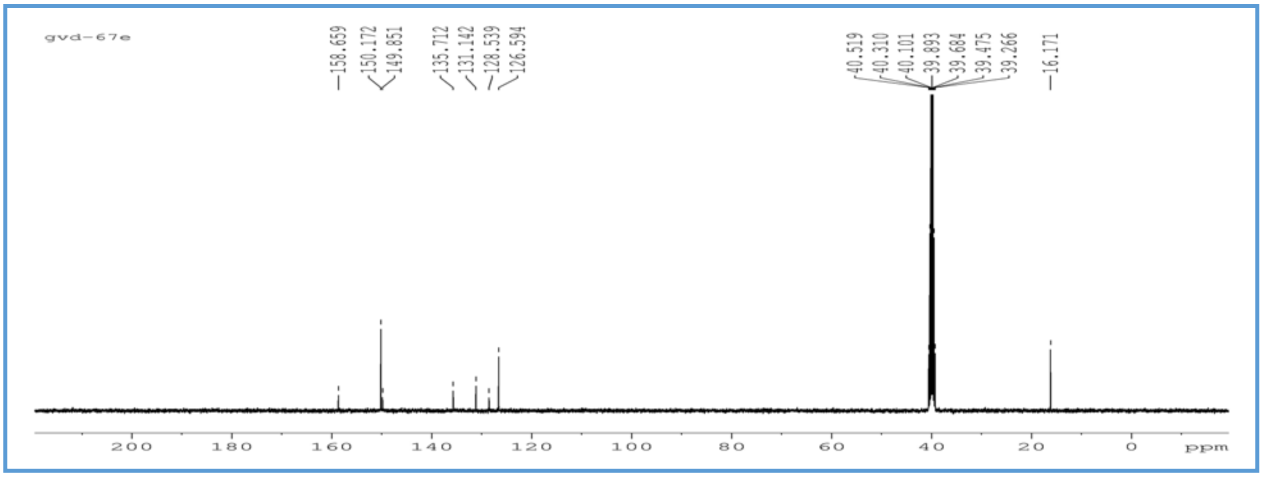


Figure 6.S22 *^{13}C NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 3-methyl-2,4,6-trinitrophenolate (**5.2d**)*

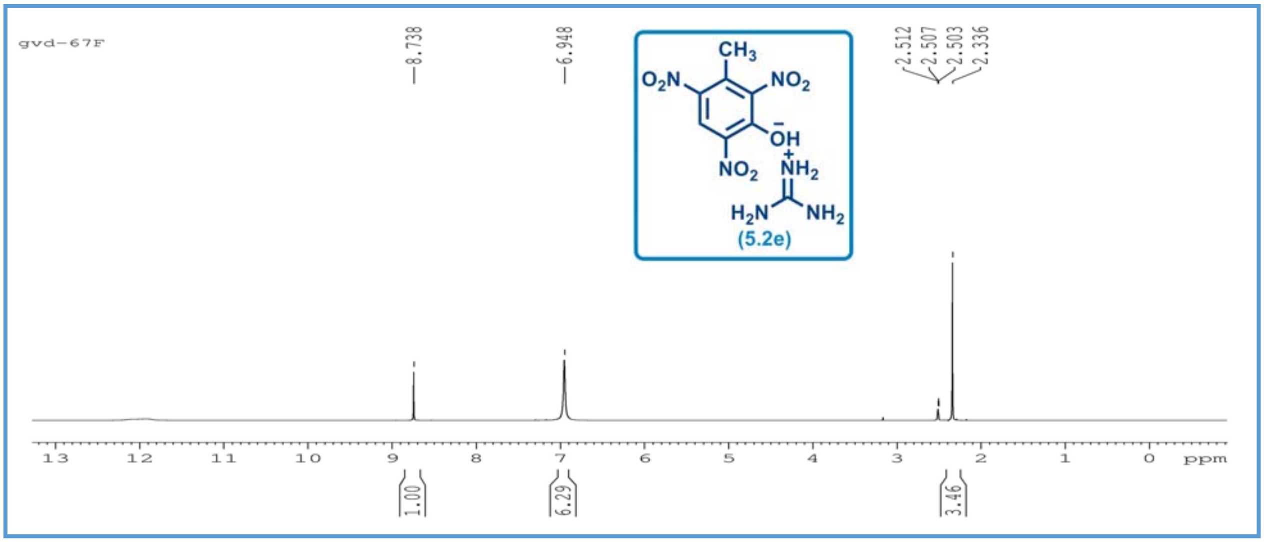


Figure 6.S23 *^{1}H NMR spectrum of Diaminomethaniminium 3-methyl-2,4,6-trinitrophenolate (**5.2e**)*

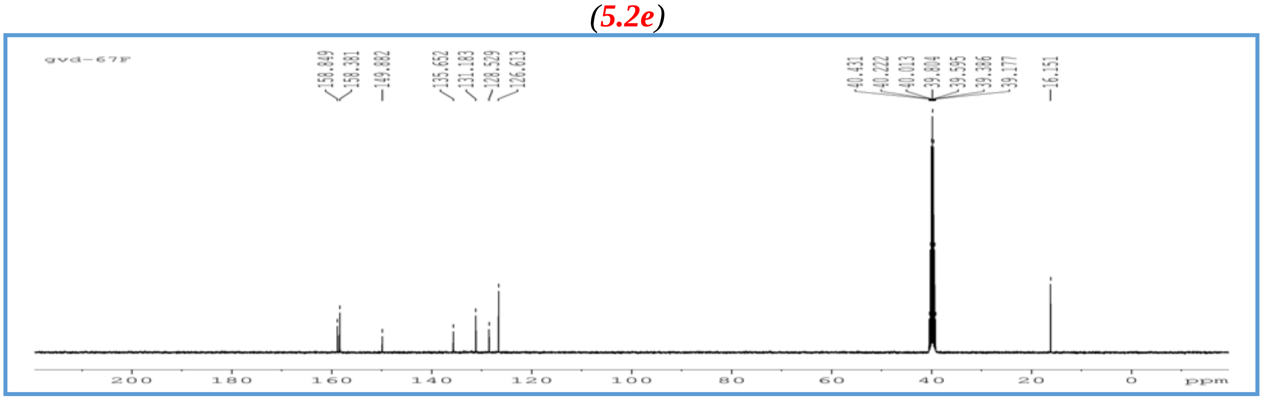


Figure 6.S24 *^{13}C NMR spectrum of Diaminomethaniminium 3-methyl-2,4,6-trinitrophenolate (**5.2e**)*

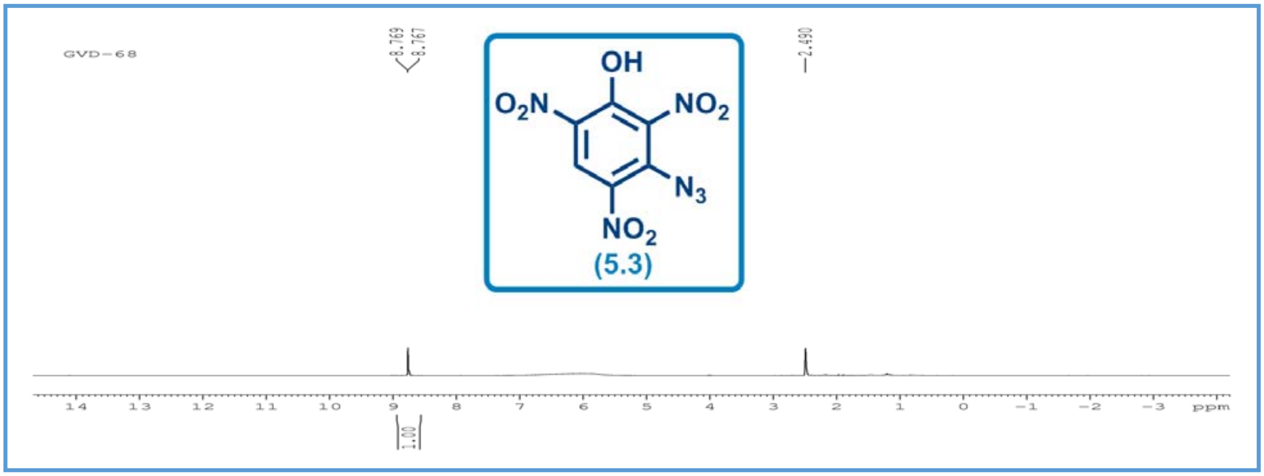


Figure 6.S25 ^{1}H NMR spectrum of 3-Azido-2,4,6-trinitrophenol (**5.3**)

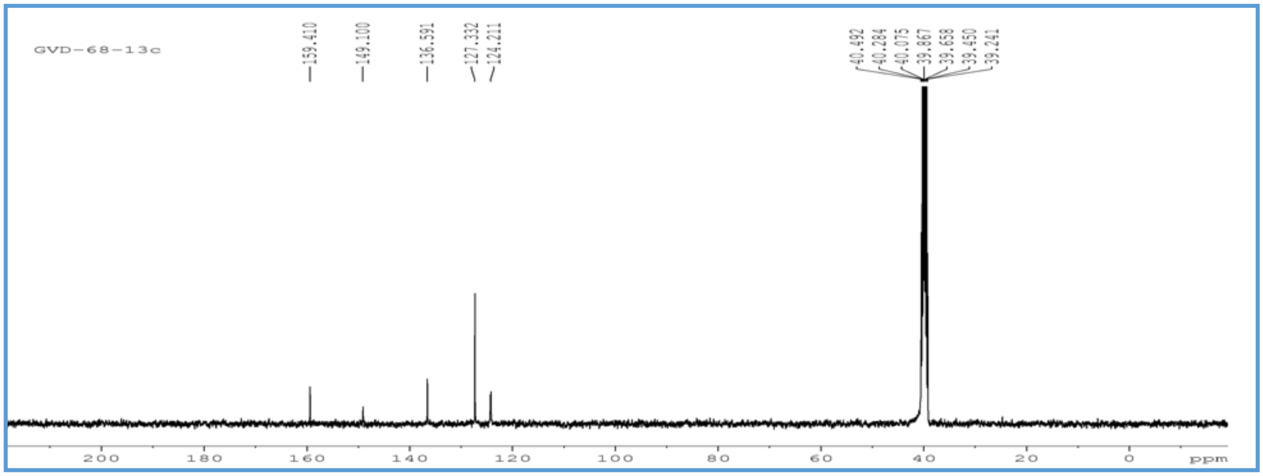
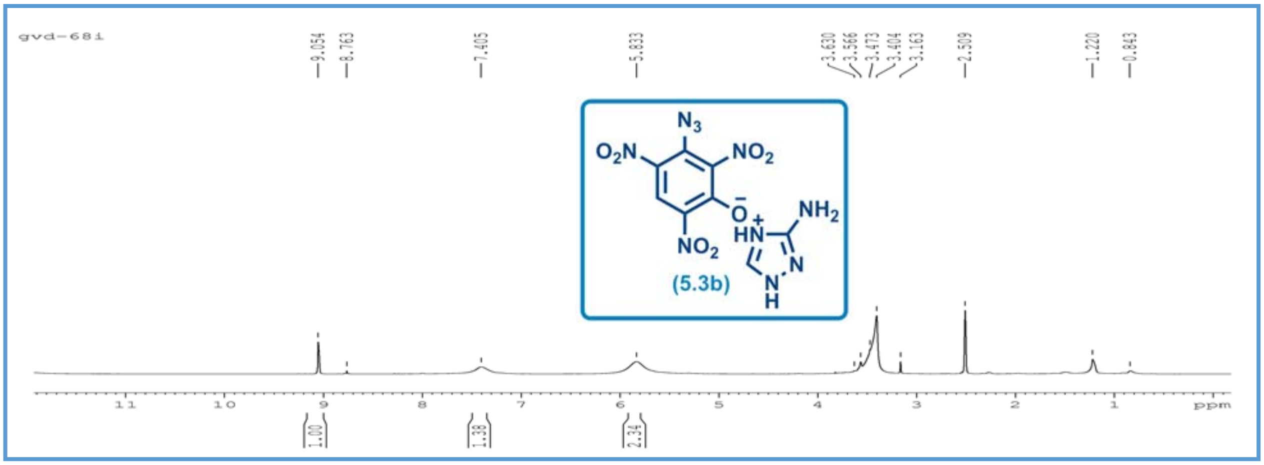


Figure 6.S26 ^{13}C NMR spectrum of 3-Azido-2,4,6-trinitrophenol (**5.3**)



igure 6.S27 ^{1}H NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (**5.3b**)

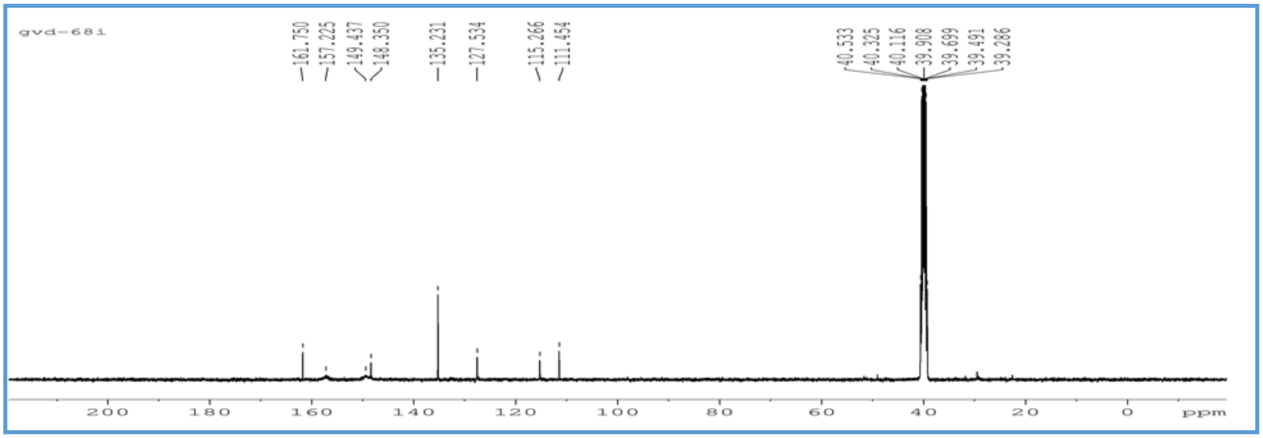


Figure 6.S28 *^{13}C NMR spectrum of 3-Amino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (**5.3b**)*

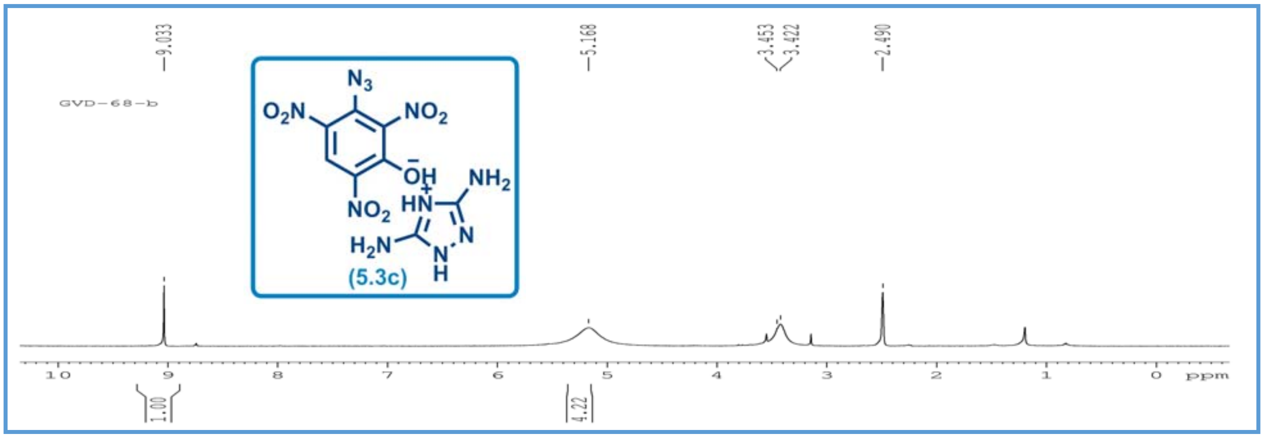


Figure 6.S29 *^{1}H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (**5.3c**)*

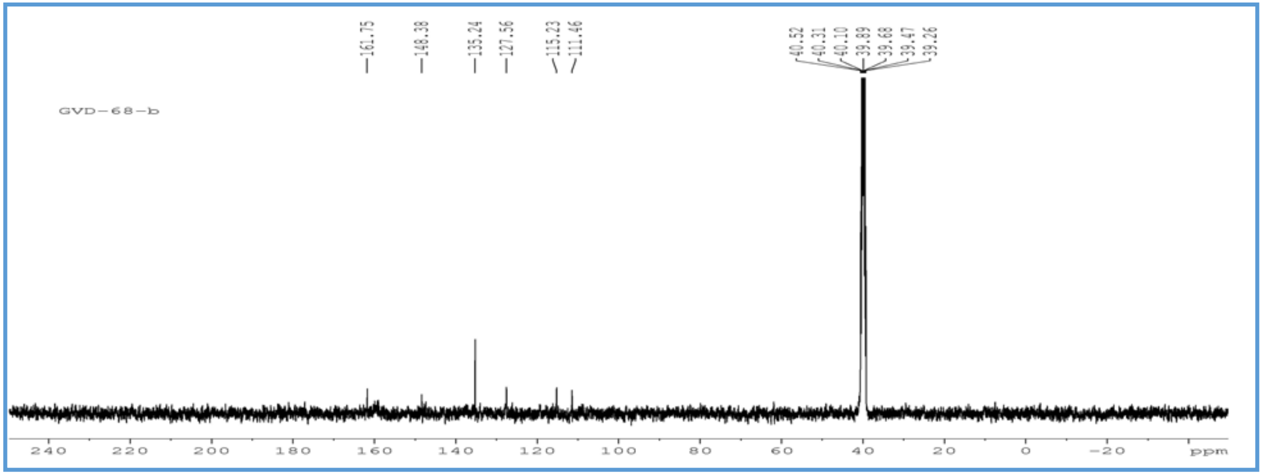


Figure 6.S30 *^{13}C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium 3-azido-2,4,6-trinitrophenolate (**5.3c**)*

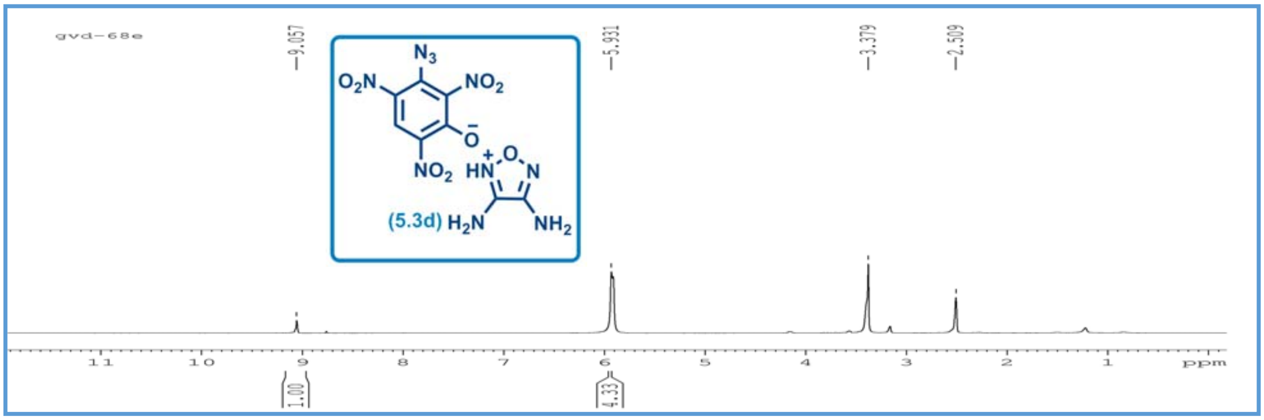


Figure 6.S31 *^{1}H NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 3-azido-2,4,6-trinitrophenolate (**5.3d**)*

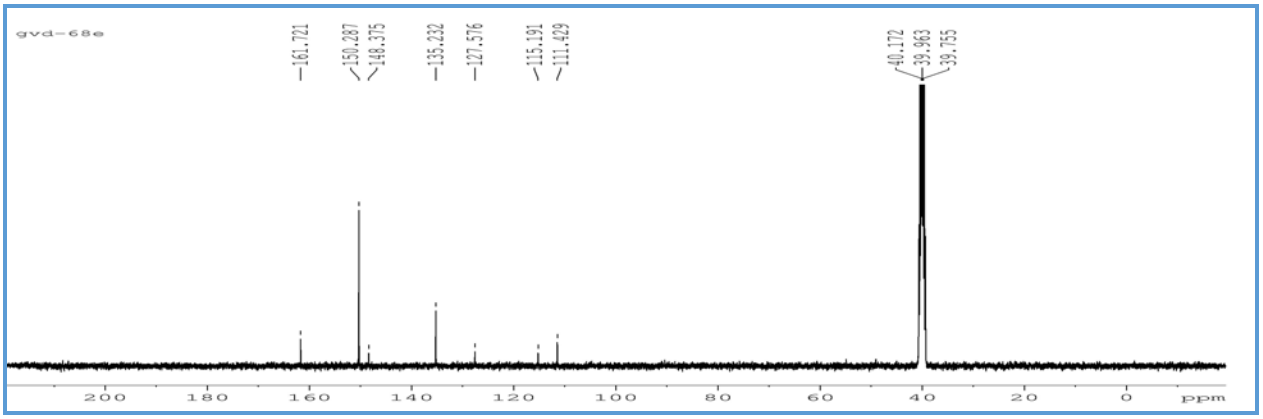


Figure 6.S32 *^{13}C NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium 3-azido-2,4,6-trinitrophenolate (**5.3d**)*

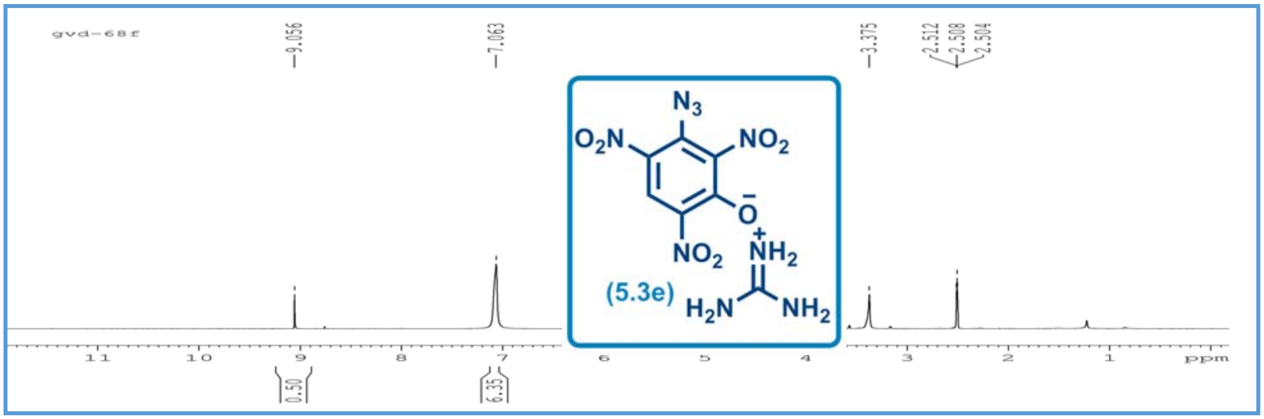


Figure 6.S33 *^{1}H NMR spectrum of Diaminomethaniminium 3-azido-2,4,6-trinitrophenolate (**5.3e**)*

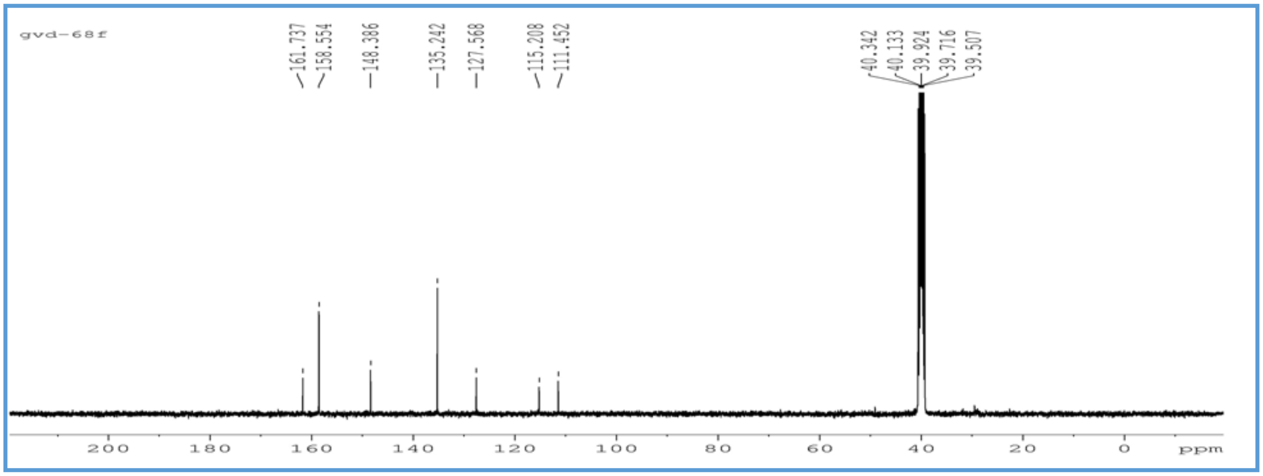


Figure 6.S34 *^{13}C NMR spectrum of Diaminomethaniminium 3-azido-2,4,6-trinitrophenolate (**5.3e**)*

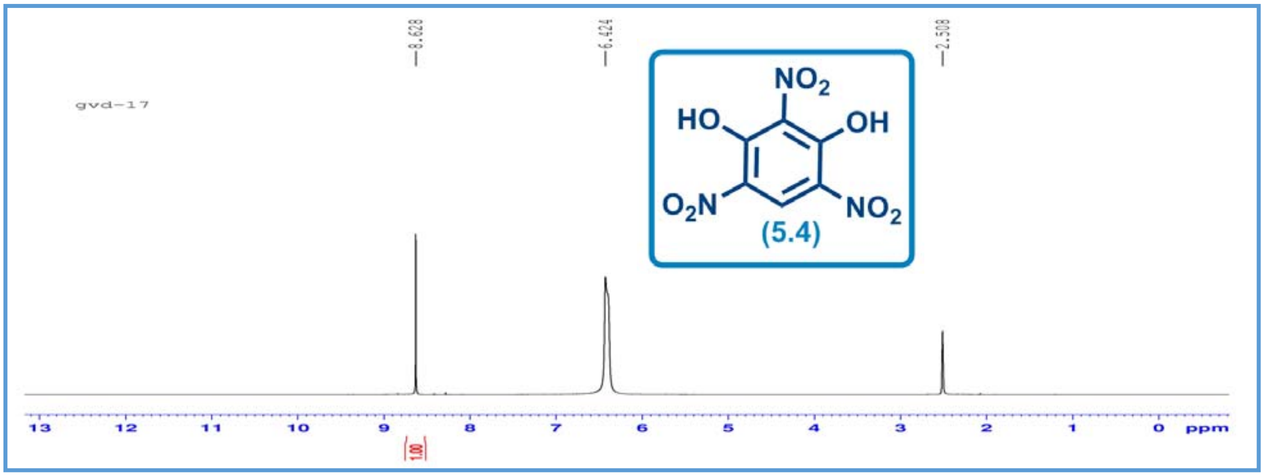


Figure 6.S35 *^{1}H NMR spectrum of Styphnic acid (**5.4**)*

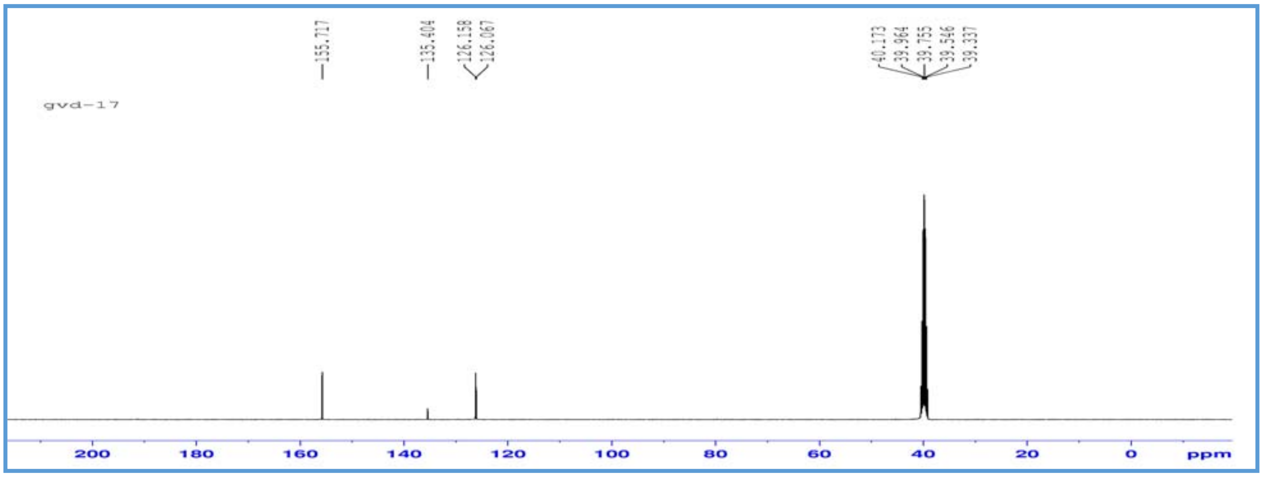


Figure 6.S36 *^{13}C NMR spectrum of Styphnic acid (**5.4**)*

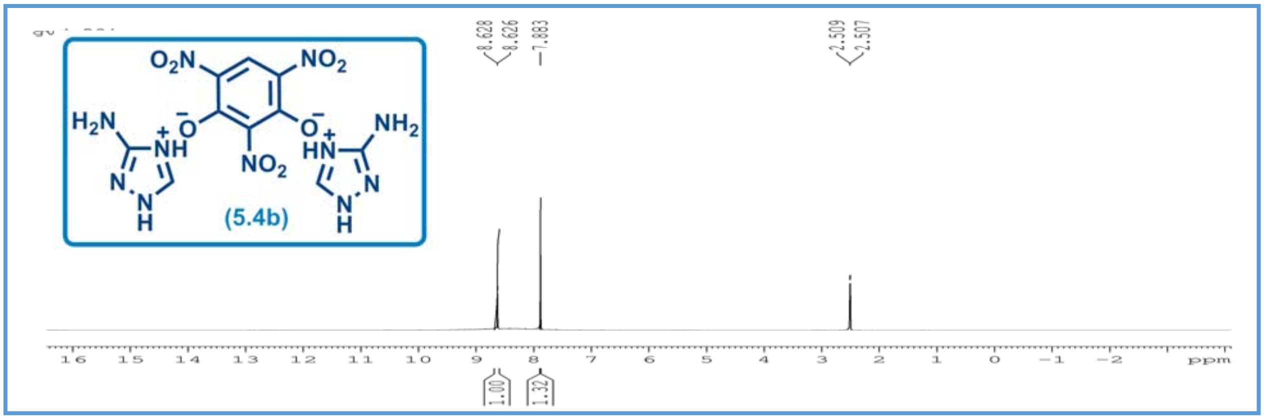


Figure 6.S37 *^{1}H NMR spectrum of Bis(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4b**)*

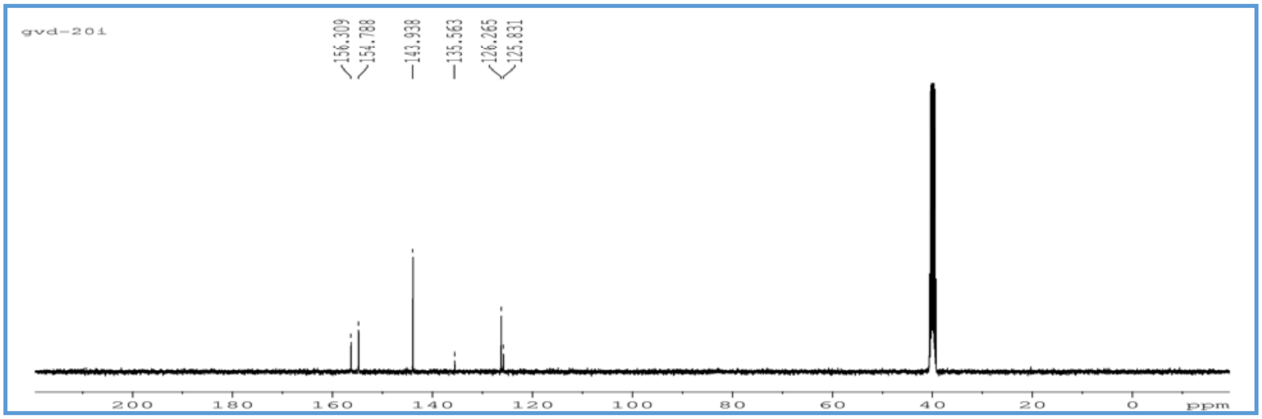


Figure 6.S38 *^{13}C NMR spectrum of Bis(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4b**)*

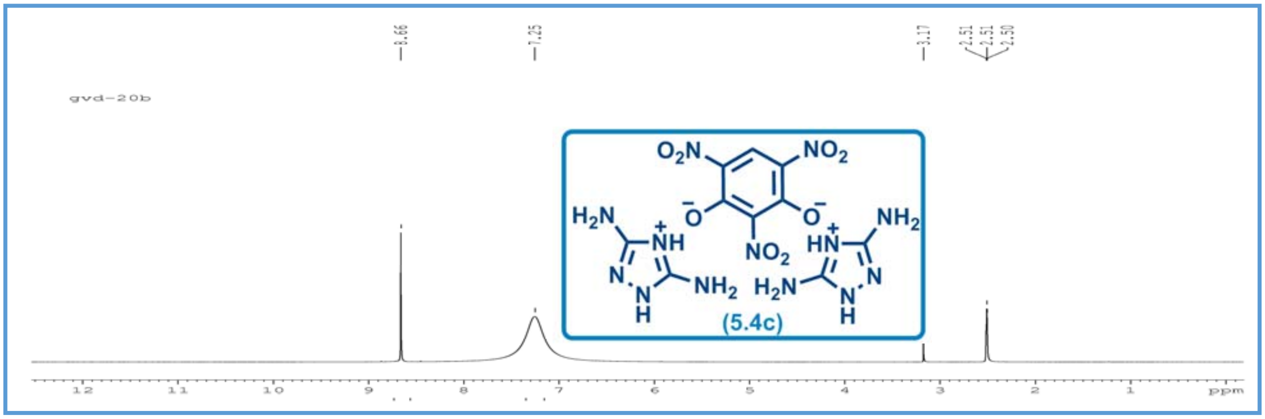


Figure 6.S39 *^{1}H NMR spectrum of Bis(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4c**)*

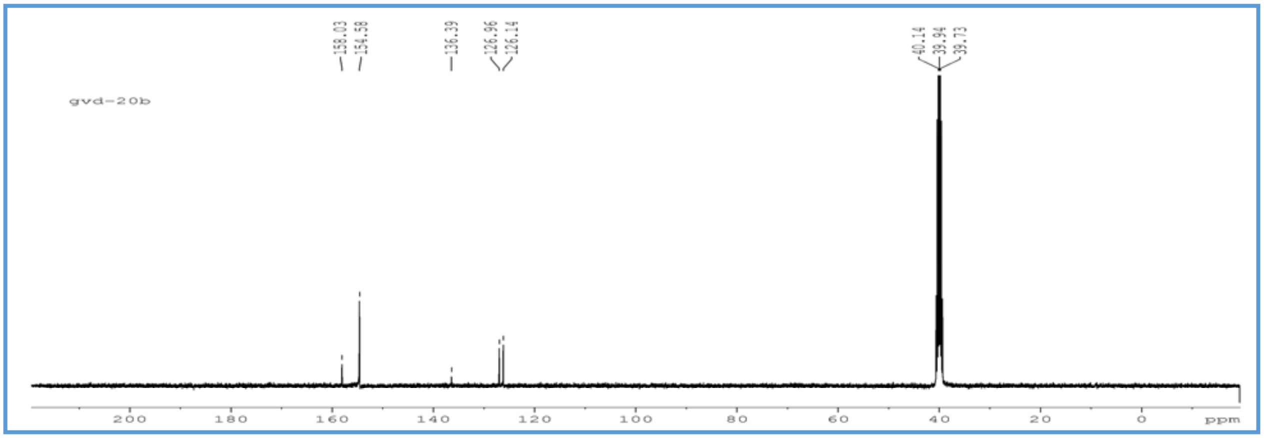


Figure 6.S40 *^{13}C NMR spectrum of Bis(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4c**)*

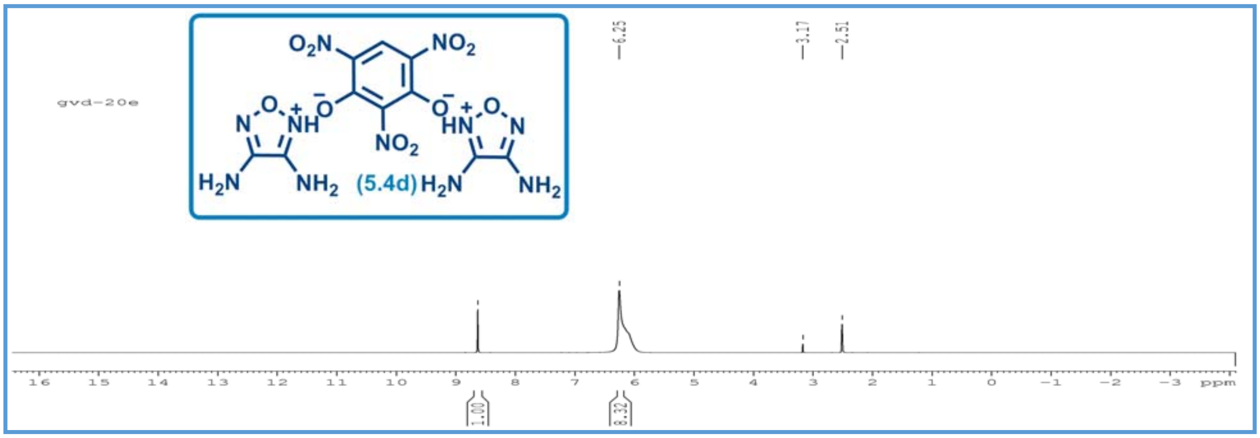


Figure 6.S41 *^{1}H NMR spectrum of Bis(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4d**)*

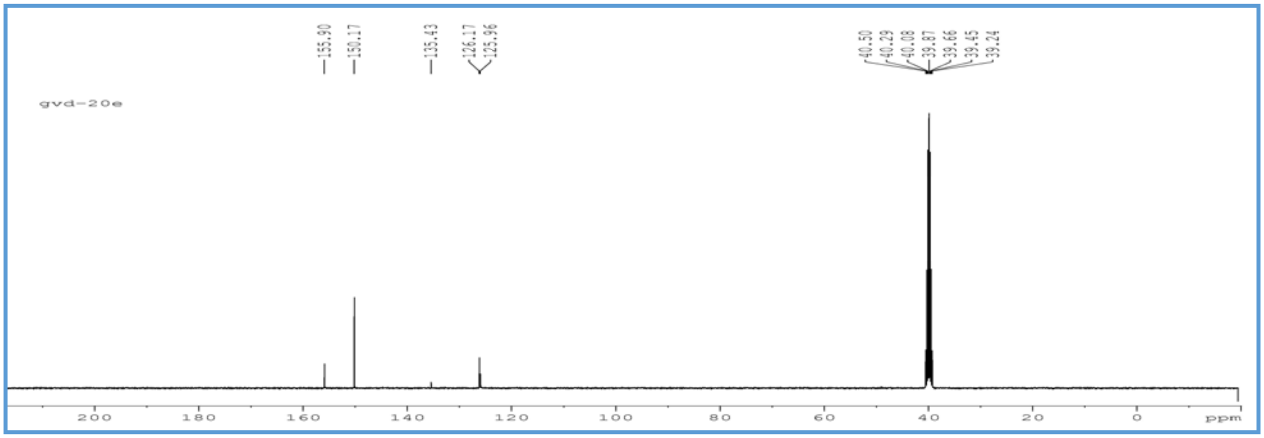


Figure 6.S42 *^{13}C NMR spectrum of Bis(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4d**)*

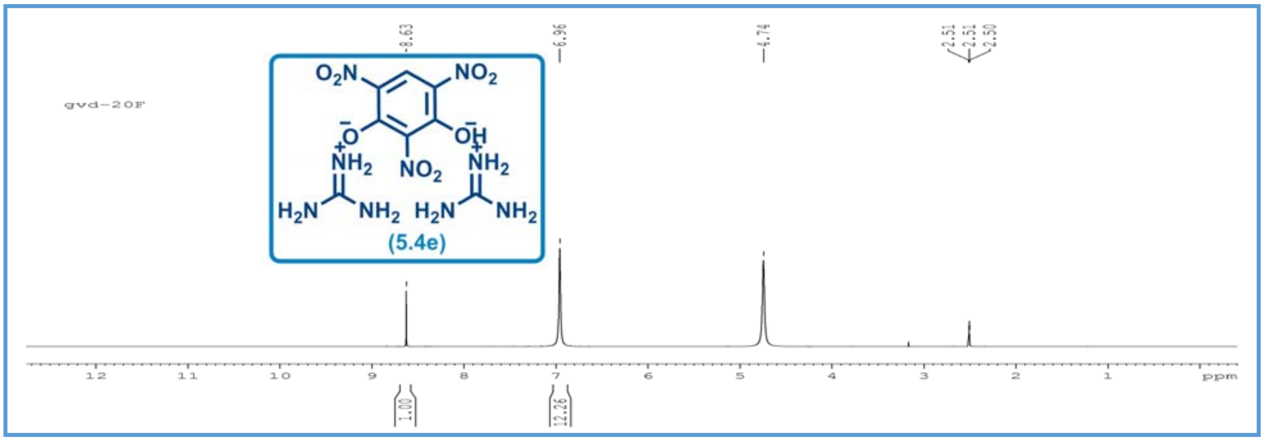


Figure 6.S43 *^{1}H NMR spectrum of Bis(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4e**)*

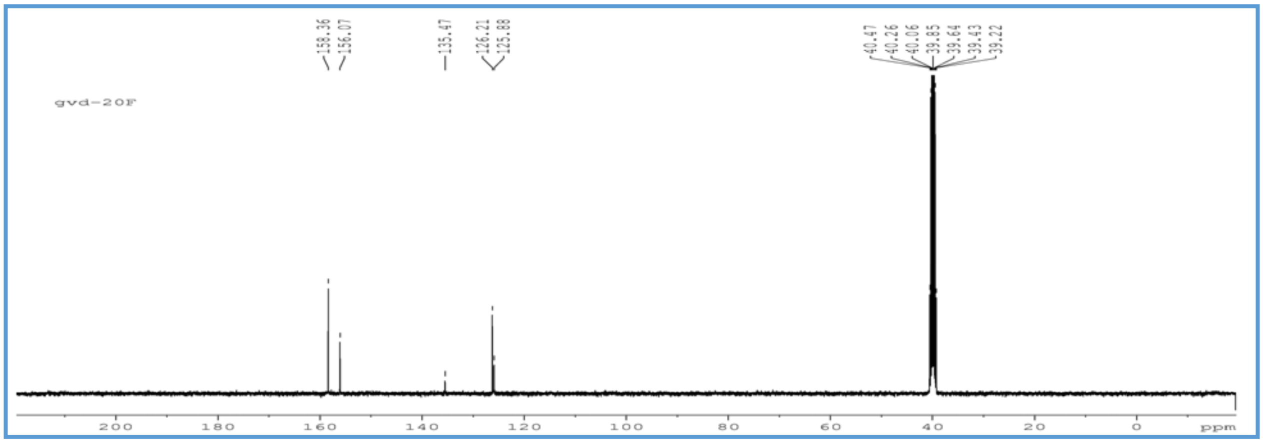


Figure 6.S44 *^{13}C NMR spectrum of Bis(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3-diolate (**5.4e**)*

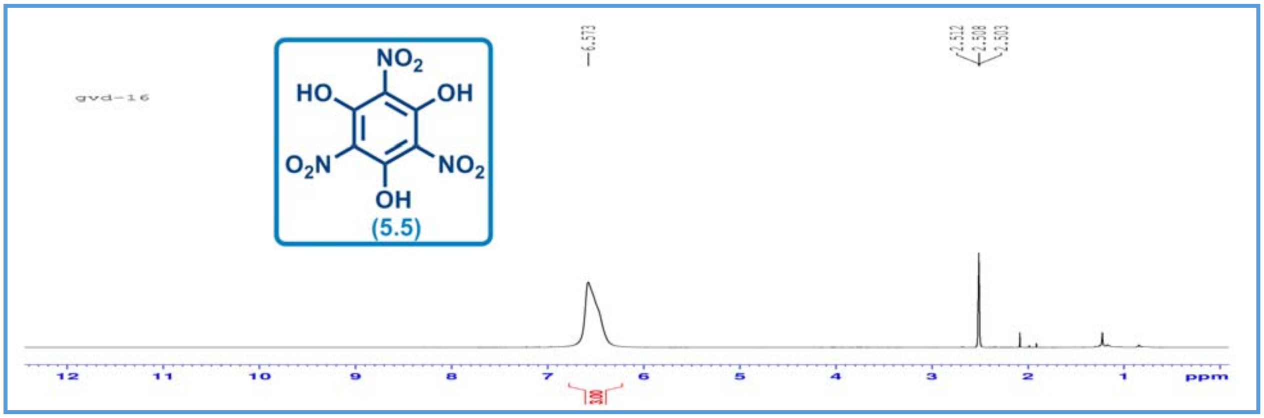


Figure 6.S45 *^{1}H NMR spectrum of 2,4,6-Trinitro-1,3,5-benzenetriol (**5.5**)*

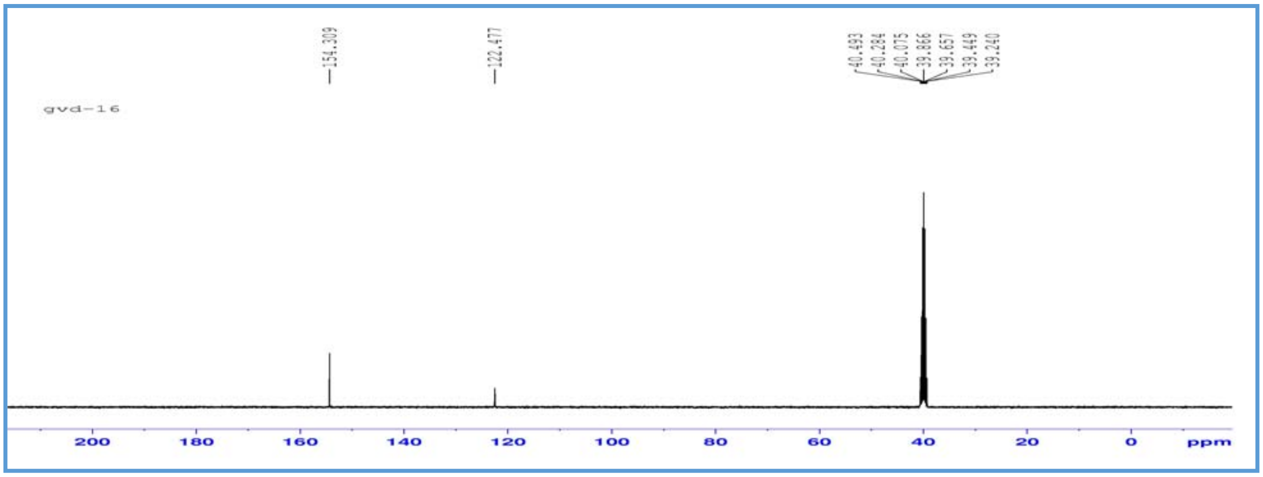


Figure 6.S46 *^{13}C NMR spectrum of 2,4,6-Trinitro-1,3,5-benzenetriol (**5.5**)*

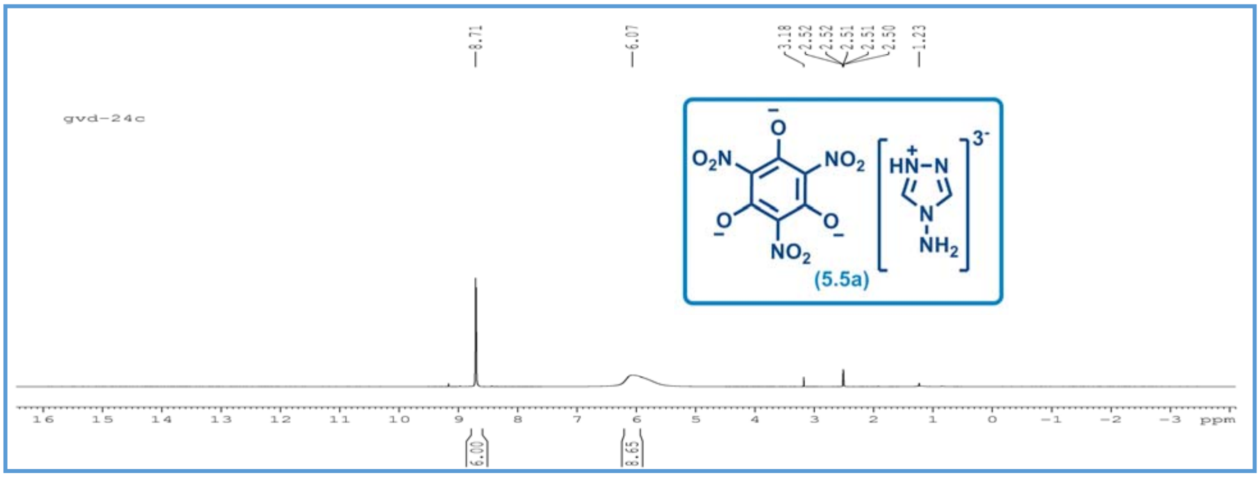


Figure 6.S47 *^{1}H NMR spectrum of Tris(4H-1,2,4-triazol-4-aminium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5a**)*

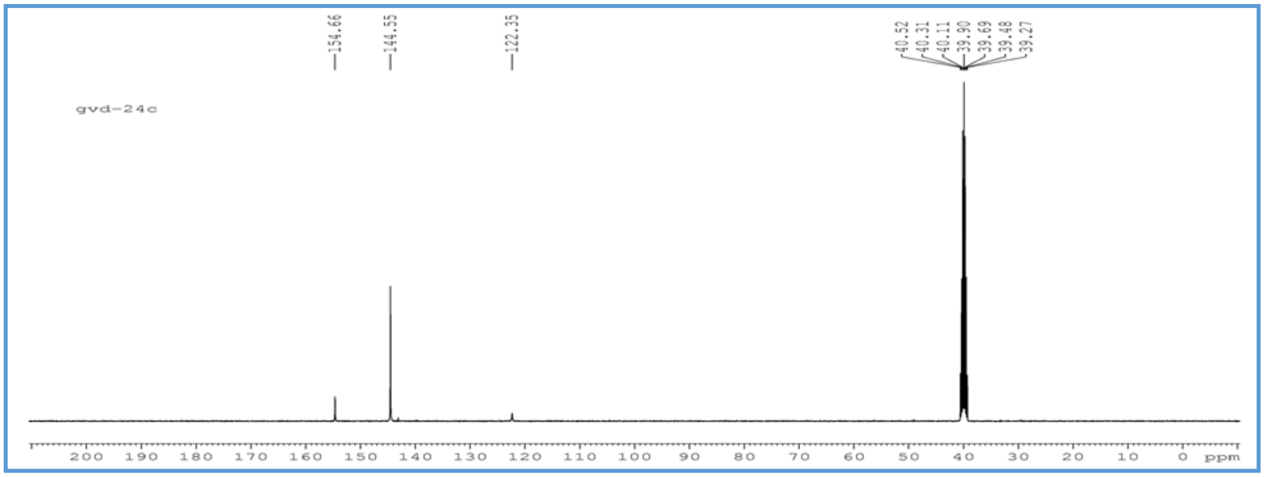


Figure 6.S48 *^{13}C NMR spectrum of Tris(4H-1,2,4-triazol-4-aminium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5a**)*

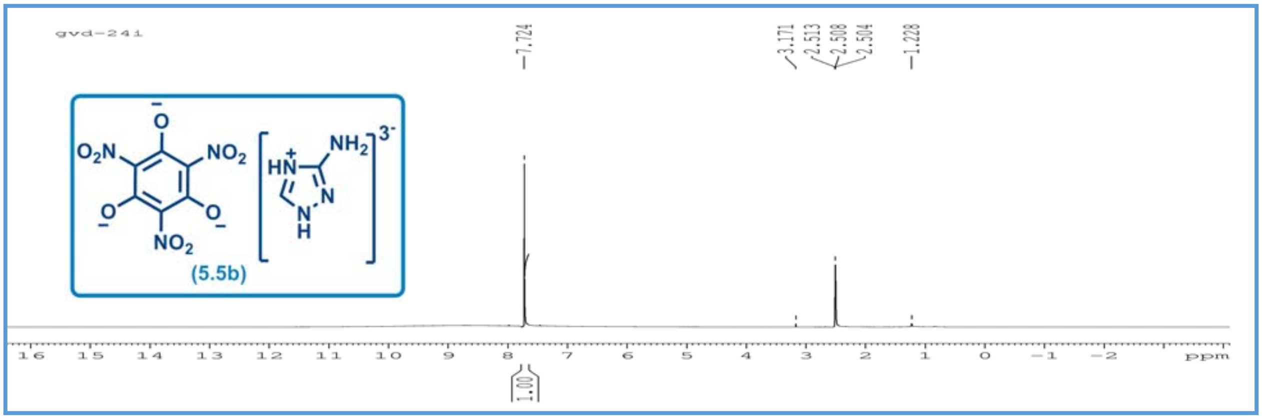


Figure 6.S49 *^{1}H NMR spectrum of Tris(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5b**)*

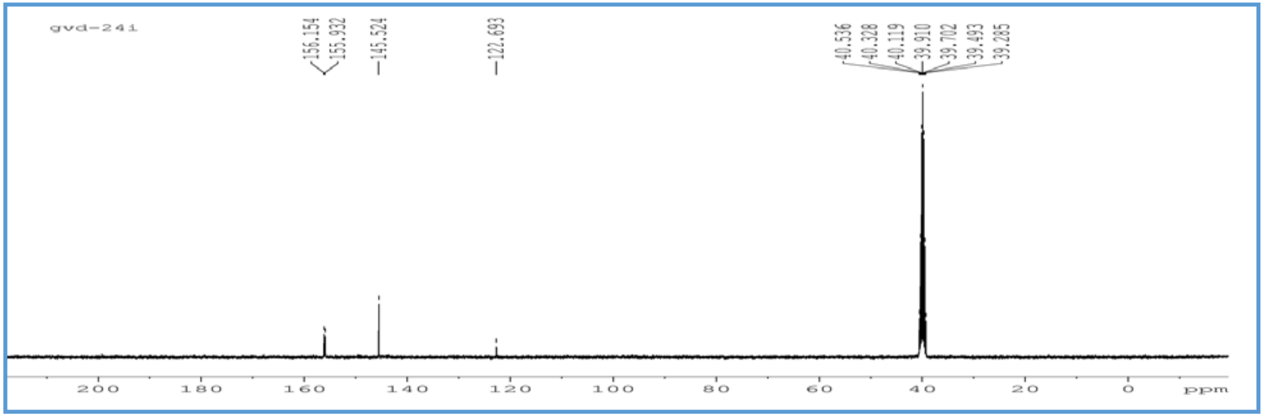


Figure 6.S50 *^{13}C NMR spectrum of Tris(3-amino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5b**)*

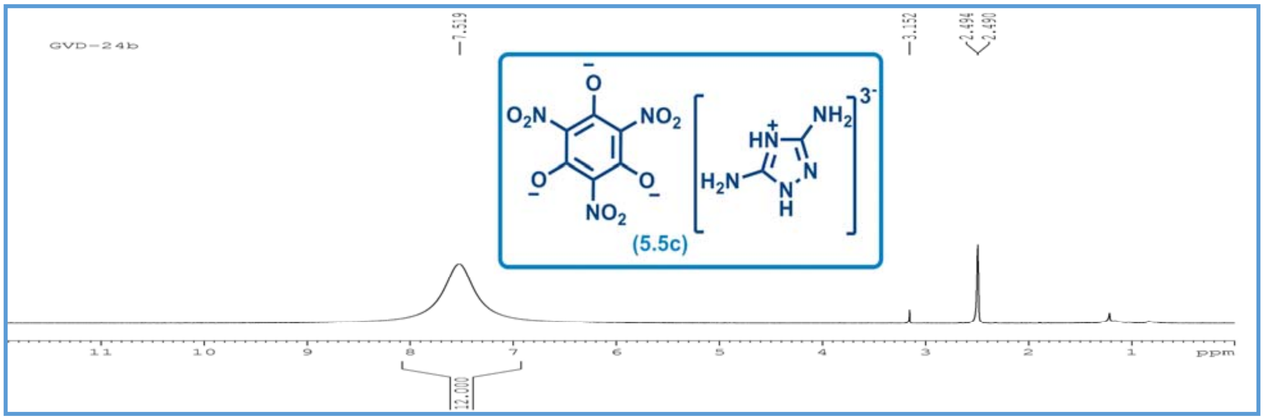


Figure 6.S51 *^{1}H NMR spectrum of Tris(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5c**)*

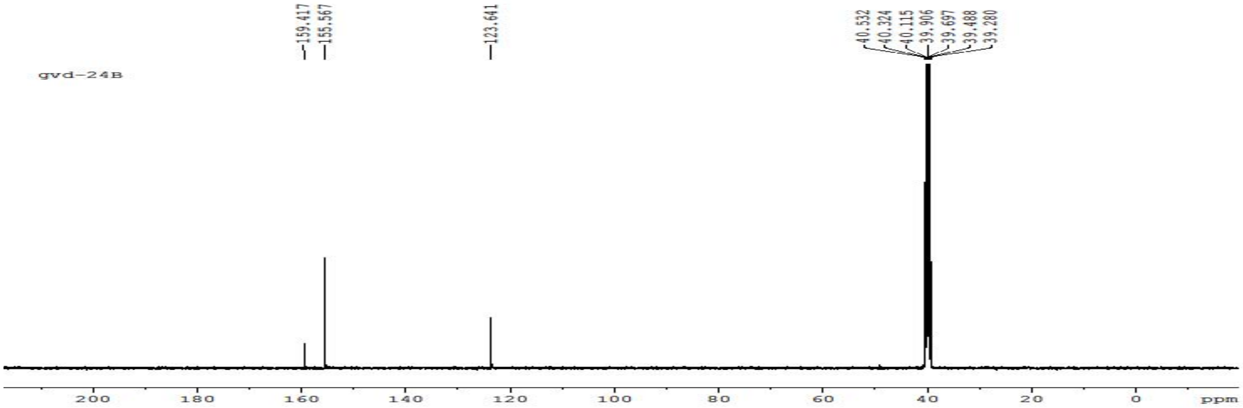


Figure 6.S52 *^{13}C NMR spectrum of Tris(3,5-diamino-1H-1,2,4-triazol-4-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5c**)*

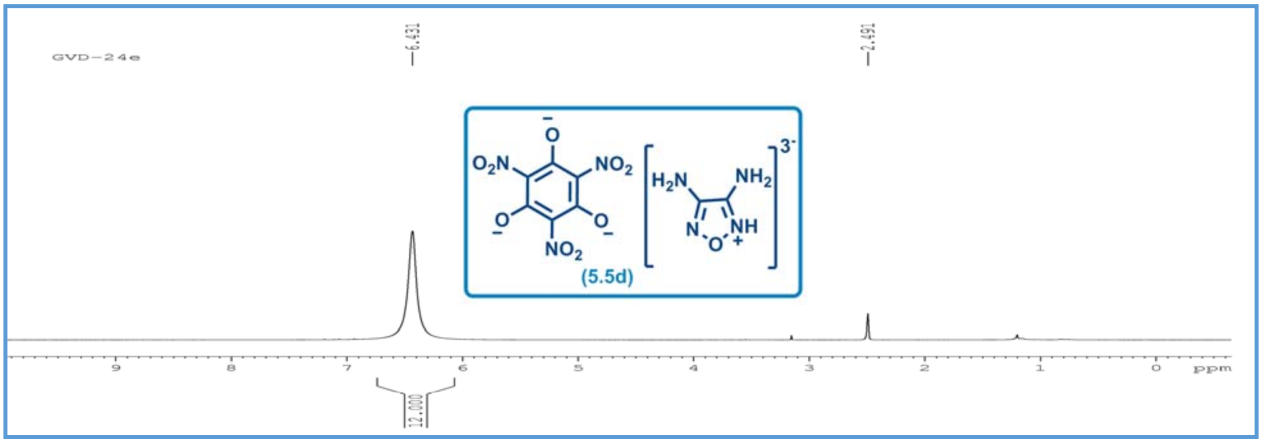


Figure 6.S53 *^{1}H NMR spectrum of Tris(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5d**)*

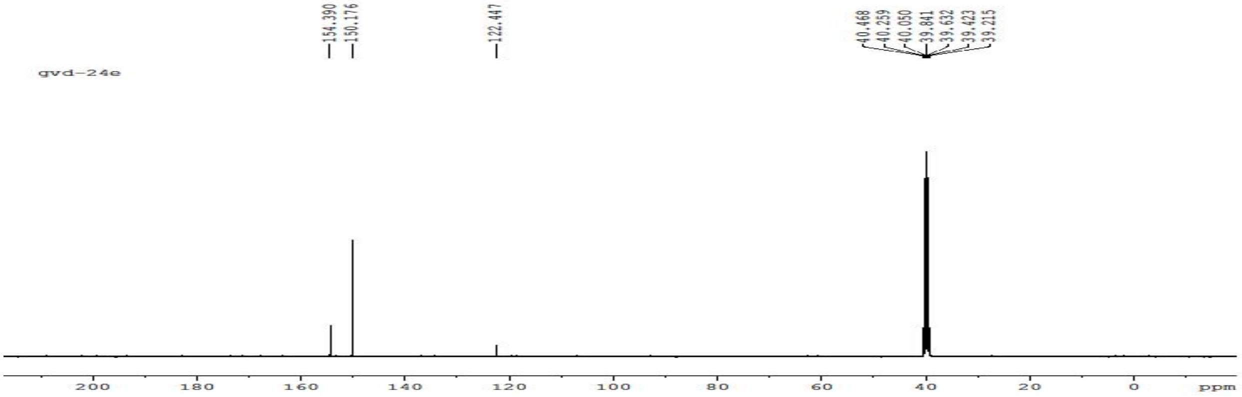


Figure 6.S54 *^{13}C NMR spectrum of Tris(3,4-diamino-1,2,5-oxadiazol-2-ium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5d**)*

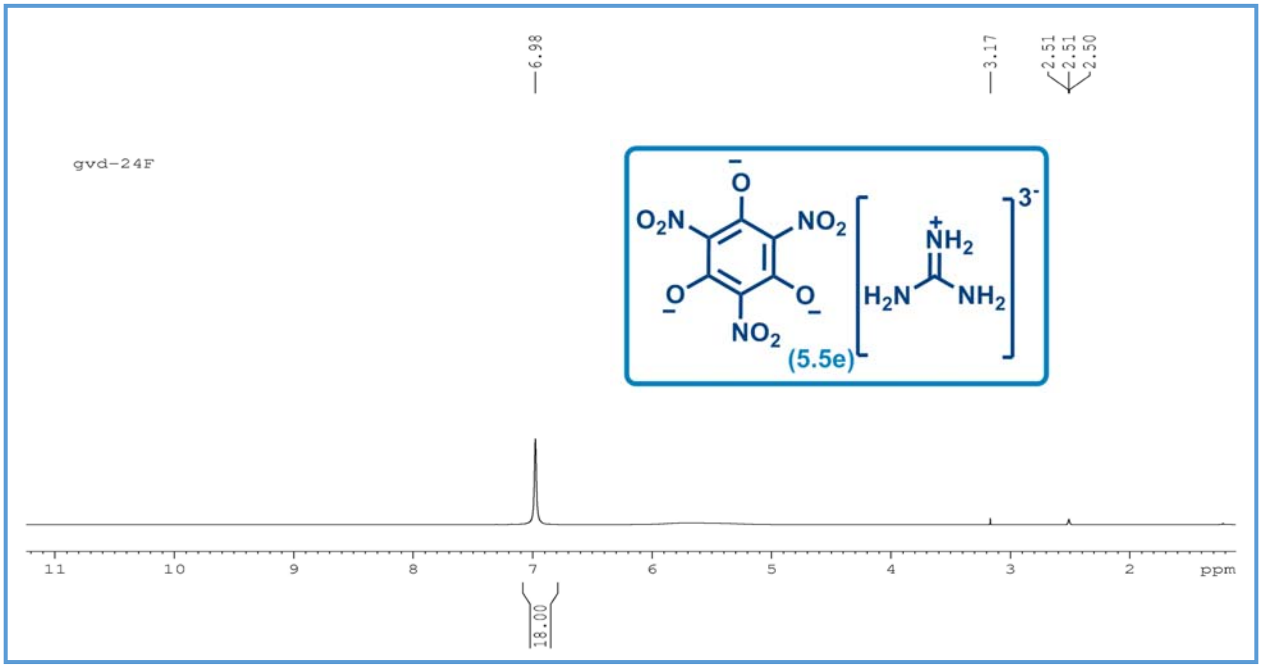


Figure 6.S55 *^{1}H NMR spectrum of Tris(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5e**)*

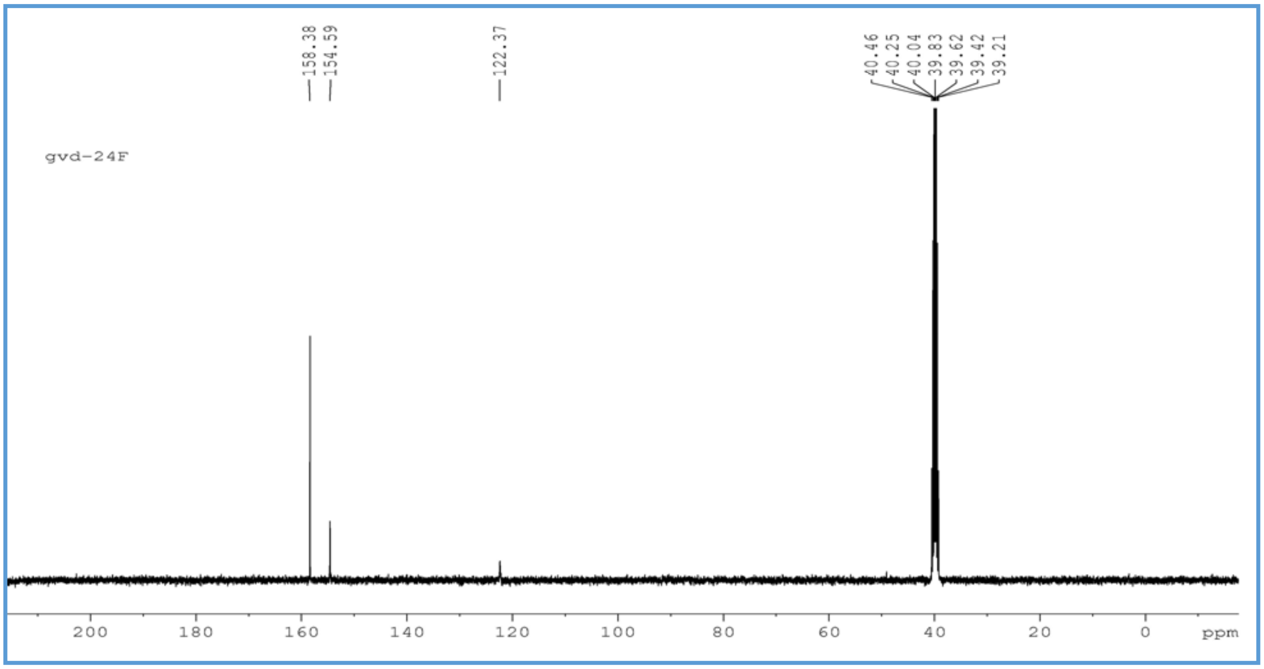


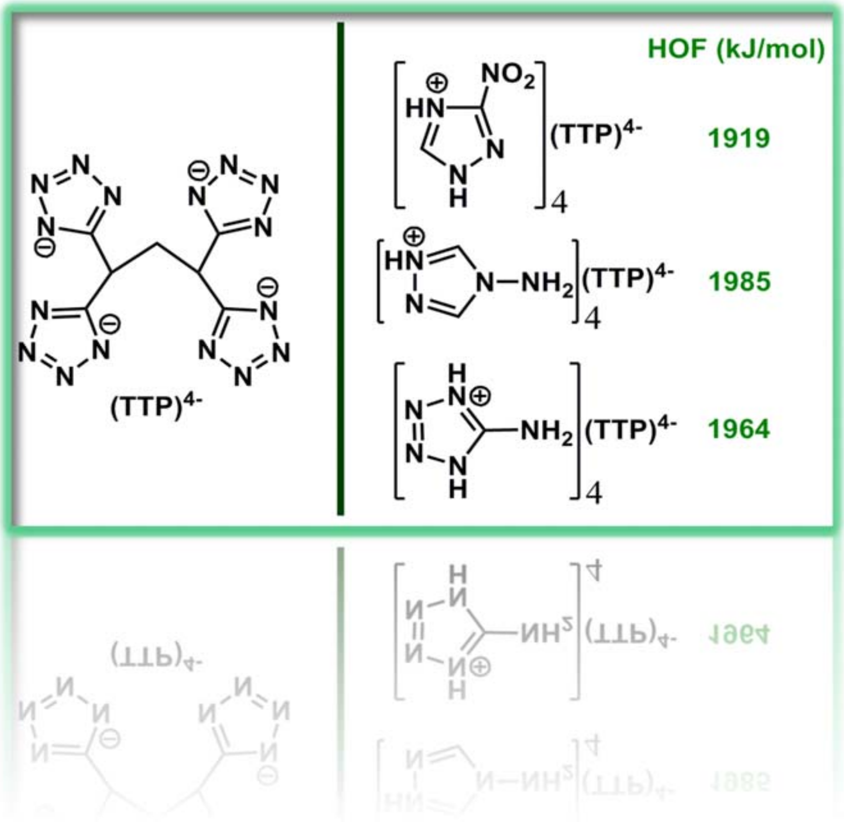
Figure 6.S56 *^{13}C NMR spectrum of Tris(diaminomethaniminium) 2,4,6-trinitrobenzene-1,3,5-triolate (**5.5e**)*

CHAPTER 6

Tetraanionic Nitrogen-Rich Tetrazole Based Energetic Salts

Abstract

1,1,3,3-Tetra(1*H*-tetrazol-5-yl)propane-based energetic salts were synthesized in a simple and straightforward manner. The structures of the new salts were determined by ^{1}H and ^{13}C NMR spectroscopy, IR, MS, and elemental analysis. All compounds show good thermal stabilities above 180 °C, as proved by TG-DTA measurements. They exhibit high positive enthalpy of formation, high nitrogen content, good thermal stability, and show moderate detonation properties.



6.1. Introduction

The synthesis and development of new energetic materials with higher performance and lower sensitivity towards thermal shock and friction has gained considerable recent interest. However, the parameters of insensitivity and high energy content are often mutually exclusive, which makes the development of new high-energy materials a challenging problem. As a consequence, attention has been devoted to nitrogen-rich heterocycles, owing to their low vapor pressures, higher enthalpies of formation, and enhanced thermal stabilities [1]. With a view to determining the structure–property relationships in energetic salts, various molecules that contained a combination of carefully selected nitrogen-rich cations and anions have been synthesized [2].

The decomposition of nitrogen-rich compounds generates large volumes of environmentally friendly N_2, which makes them promising candidates for applications that require environmental friendly and "green" energetic materials. Among the various types of five-membered nitrogen-containing heterocycles, tetrazoles can be easily deprotonated to give tetrazolates and they have been found to be an interesting class of high-energy materials [3]. Tetrazole-based energetic materials combine several advantages, including smokeless combustion, high positive enthalpies of formation, and high propulsive power, which allows them to take on a significant role in modern propellants, explosives, and pyrotechnics [4]. In addition, the properties of tetrazole-based salts can be readily modified by varying the substituents on them and, furthermore, the preparation of tetrazole-based halogen-free energetic salts can be achieved by a facile synthetic process. This process provides a powerful method for the design of high-energy materials that can be tailored to specific applications.

With the aim of using the advantageous properties of tetrazoles and to study their structure–property relationships, we have synthesized a variety of its derivatives. Herein, we report the synthesis, characterization, and energetic properties of nitrogen-rich energetic tetraanionic salts of 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane (**TTP**).

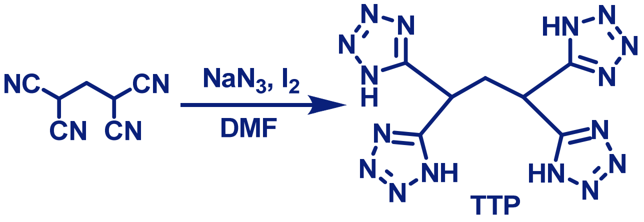
6.2. Results and discussion

6.2.1. Synthesis and characterization

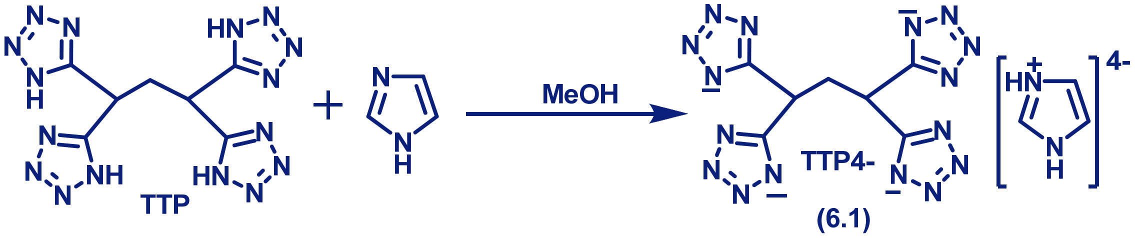
The introduction of multiple heterocycles that contain different explosophores within a single cation has been found to lead to promising energetic properties [5]. Hence, we have synthesized a series of 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane (**TTP**) salts, which was accompanied by an increase in nitrogen content. The interest in these TTP salts stemmed from the high nitrogen content (71%), the high predicted positive enthalpy of formation (1045 $kJmol^{-1}$), and the excellent thermal stability of TTP (about 276 °C). TTP can be synthesized according to a literature procedure [6] by the reaction of propane-1,1,3,3-tetracarbonitrile with sodium azide in the presence of zinc bromide. We have successfully prepared TTP with an improved yield from the same reaction but in the presence of iodine (Scheme 6.1). Two important key requirements for the practical application of an energetic material are 1) that its synthesis must be simple and 2) that the starting materials should be inexpensive. The starting material propane-1,1,3,3-tetracarbonitrile fulfills these conditions and the overall yields of the various products were good.

To determine the correlation between the structure and properties in these TTP salts, various cations were selected and are shown in Scheme 6.2-6.12. The reactions of TTP with four molar equivalents of imidazole, 4-nitroimidazole, 4-amino- 4*H*-1,2,4-triazole, 1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5- diamino-1,2,4-triazole, 3-nitro-1,2,4-triazole, 3,4-diaminofurazan, 5-aminotetrazole, melamine, 2,4,6-trinitroaniline, and guanidine in MeOH resulted in the formation of target tetraanionic salts **6.1–6.12**. Upon the addition of any of these molecules, deprotonation of the NH moiety of the tetrazole in TTP occurs and a highly aromatic tetrazolate anion is formed, thus yielding the corresponding energetic salts. Surprisingly, the reaction of TTP with carbohydrazide and urea under similar conditions did not occur; thus, the corresponding salts could not be prepared by this route. The structures of these new salts were determined by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, MS, and elemental analysis.

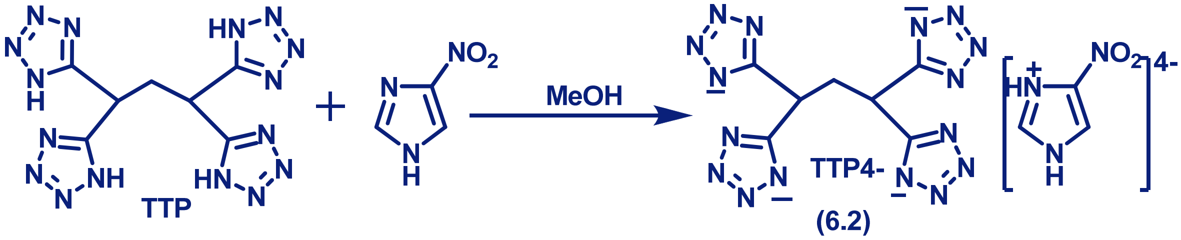
All of the new energetic **TTP** salts were nonhygroscopistable in air, and could be stored at ambient temperature. As shown in Table 6.1, all of these salts exhibited excellent thermal stabilities, which could be attributed to extensive and strong hydrogen-bonding interactions between the cations and the anions. The decomposition temperatures of these salts fell within the range 180– 296 °C, whilst that of TTP was 276 °C. Compounds **6.2, 6.9, 6.10, 6.12,** and TTP decomposed without melting.



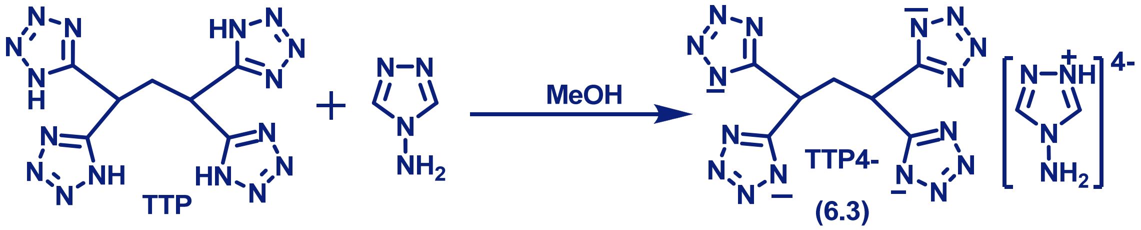
Scheme 6.1 Synthesis of 1,1,3,3-tetra(1H-tetrazol-5-yl)propane



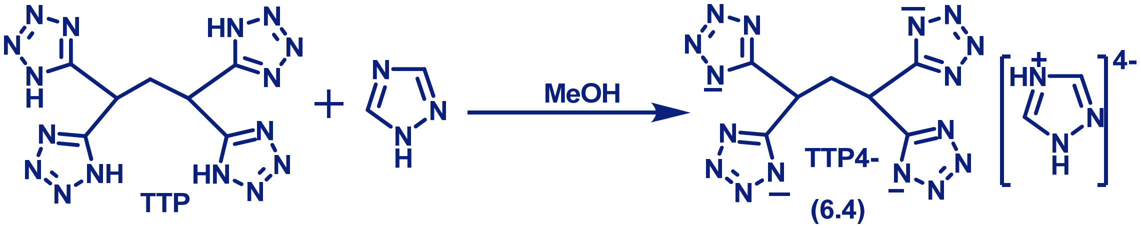
Scheme 6.2 Synthesis of 1H-Imidazol-3-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.1)



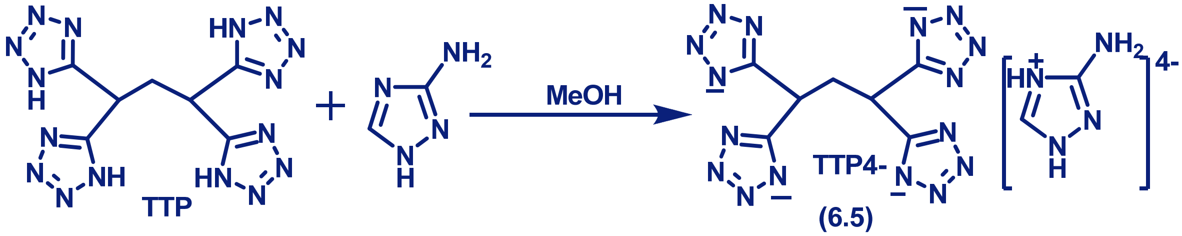
Scheme 6.3 Synthesis of Tris(4-nitro-1H-imidazol-3-ium)-5-nitro-1H-imidazol-3-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.2)



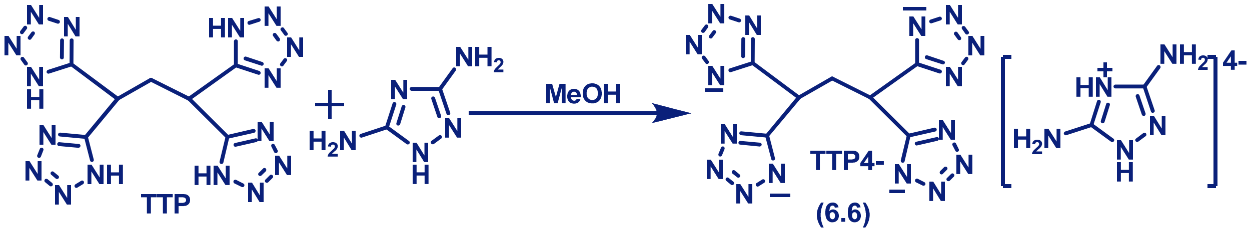
Scheme 6.4 *Synthesis of 4H-1,2,4-Triazol-1-aminium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.3)*



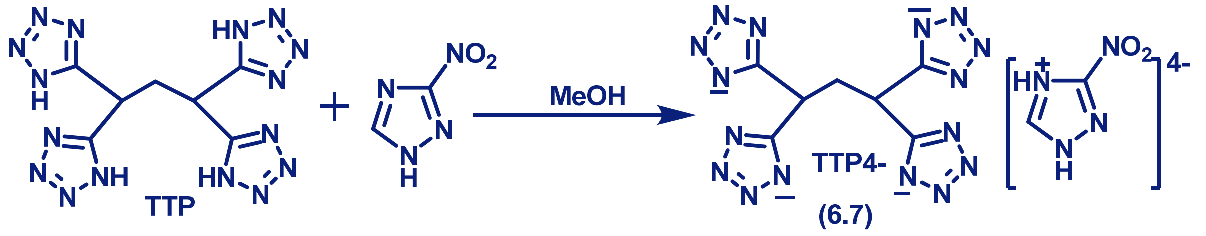
Scheme 6.5 *Synthesis of 1H-1,2,4-Triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.4)*



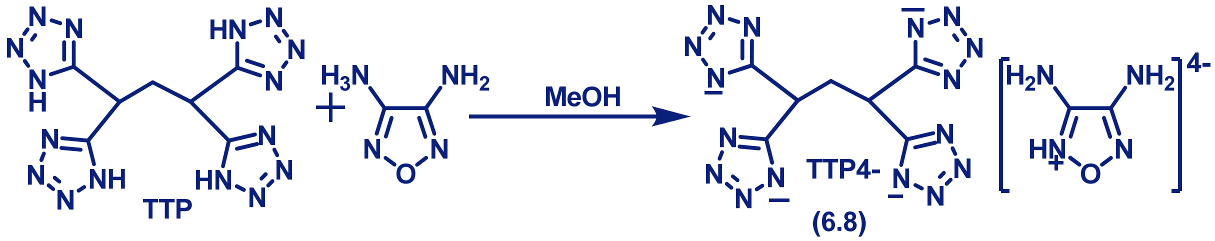
Scheme 6.6 *Synthesis of 3-Amino-1H-1,2,4-triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.5)*



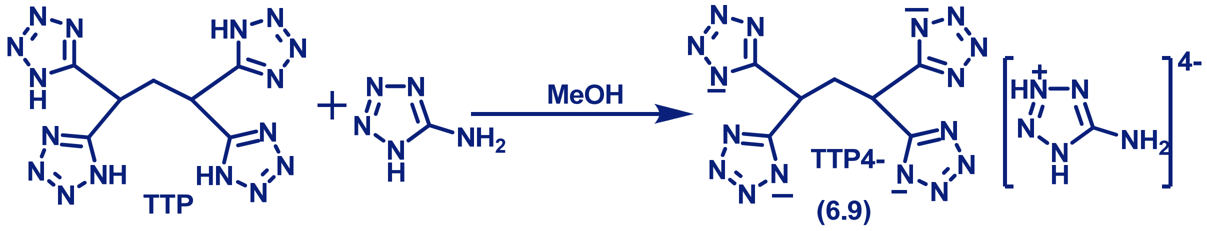
Scheme 6.7 *Synthesis of 3,5-Diamino-1H-1,2,4-triazol-4-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetr-azol-1-ide (6.6)*



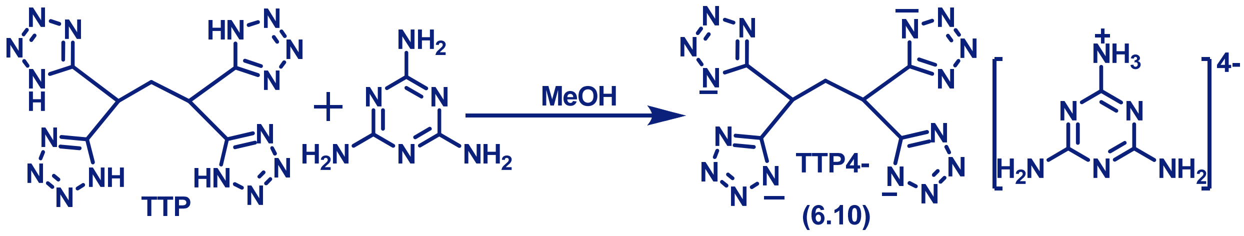
Scheme 6.8 *Synthesis of 3-Nitro-1H-1,2,4-triazol-4-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.7)*



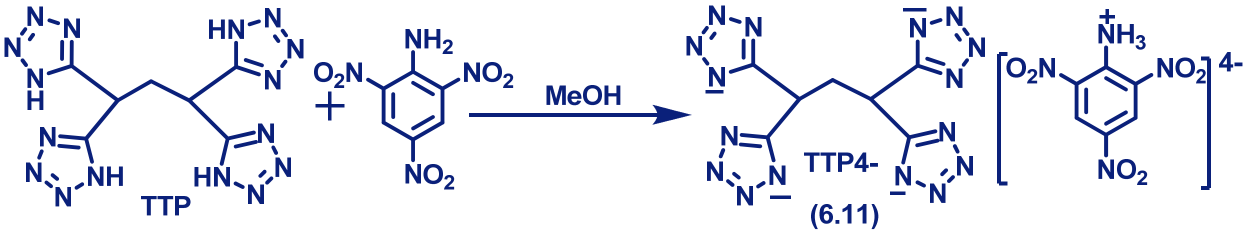
Scheme 6.9 *Synthesis of 3,4-Diamino-1,2,5-oxadiazol-2-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetra -zol-1-ide (6.8)*



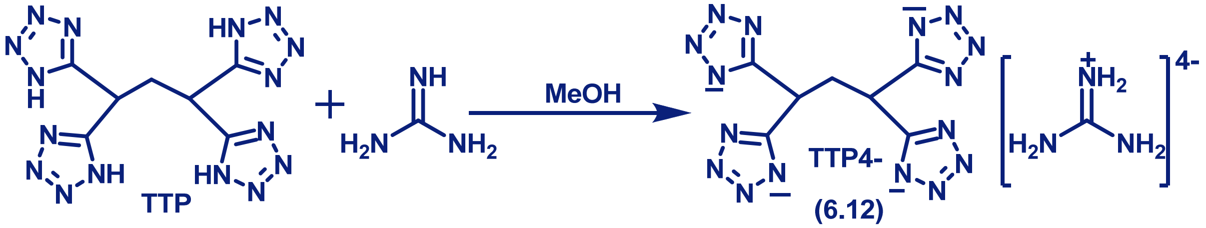
Scheme 6.10 *Synthesis of 5-amino-1H-tetrazol-2-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.9)*



Scheme 6.11 *Synthesis of 4,6-Diamino-1,3,5-triazin-2-aminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)titrate-trazol-1-ide (6.10)*



Scheme 6.12 Synthesis of 2,4,6-Trinitrobenzenaminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.11)



Scheme 6.13 Synthesis of Diaminomethaniminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.12)

6.2.2. Energetic Properties

The enthalpy of formation (HOF) of an energetic material provides information regarding its energy content and is important in assessing its detonation performance. To obtain energetic salts with high energy, the anions should also possess high positive HOFs. The gas-phase HOFs were calculated by using a computational approach through isodesmic reactions. The HOFs for TTP and compounds **6.1–6.12** were calculated based on the Born Fajans–Haber enthalpy cycles (Figure 6.1) and are summarized in Table 6.1. The calculated HOF of TTP (1045 $kJmol^{-1}$) was positive, which can be attributed to the high energy contribution from the four tetrazole groups. The HOFs exhibited by these energetic salts were within the range 319–1984 $kJmol^{-1}$. Nitrogen-containing heterocycles are one of the sources of energy content in these salts. The HOFs of the 4-amino-4*H*-1,2,4-triazole (**6.3**), 3-nitro-1,2,4-triazole (**6.7**), and 5-aminotetrazole (**6.9**) salts were found to be higher (>1900 $kJmol^{-1}$) than those of the other salts. A comparison of salts **6.1** and **6.2** showed that the substitution of a nitro group onto the imidazole ring improved the HOF and a similar trend was observed by comparing 1,2,4-triazole salts **6.4** and **6.7**.

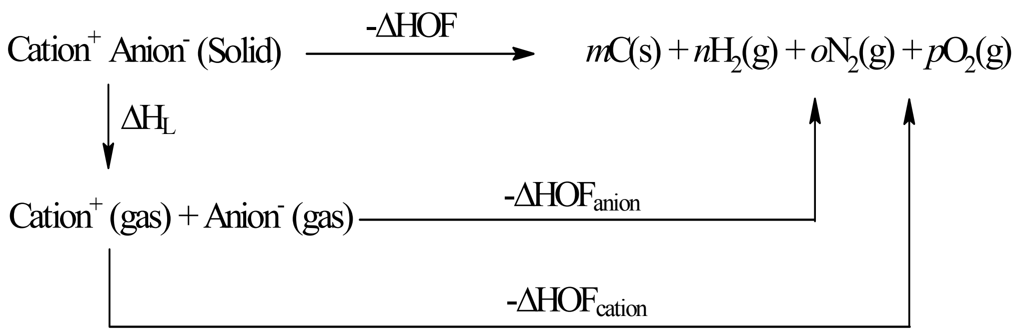


Figure 6.1. *Born–Fajans–Haber cycle for the formation of energetic salts (DHL=lattice enthalpy for ionic salts; DHOFcation and DHOFanion=enthalpy of formation of the cation and anion, respectively).*

A comparison of the HOFs of salts **6.4, 6.5**, and **6.6** clearly shows that the introduction of an amino group(s) decreases the HOFs of the respective compounds by 70–80 $kJmol^{-1}$. The high positive HOFs are directly attributable to the large number of inherently energetic N-N and C-N bonds in the molecular framework. Density is one of the most important factors in determining the performance of energetic compounds. The densities of salts **6.1–6.12** were calculated by using the Hofmann approach [7] and fell within the range 1.49– 1.71 gcm^{-3} (Table 6.1). The presence of a nitro group played an important role in increasing the density of the corresponding salt and, hence, salts **6.7** and **6.11** possessed the highest densities (1.71 and 1.70 gcm^{-3}, respectively). Because of the flat structure of the tetrazole ring and its high nitrogen content, its corresponding compounds had high densities, thus releasing considerable energy and gases upon decomposition/ explosion.[5]

From the calculated HOFs and densities of these new energetic salts, their detonation velocities (*VOD*) and detonation pressures (*DP*) were calculated by using the Kamlet–Jacobs equation [8]. The detonation velocities fell within the range **5–8** kms^{-1} and their detonation pressures were between 10– 25 GPa (Table 6.1). Salts **6.7** (*VOD*=7.53 kms^{-1}, *DP*=24.41 GPa) and **6.11** (*VOD*=7.51 kms^{-1}, *DP*=24.13 GPa) exhibited better detonation performance than TNT (*VOD*=7.21 kms^{-1}, *DP*= 22.49 GPa). Overall, these salts possessed high nitrogen content, high positive HOFs, and moderate performance.

Table 6.1. *Properties of energetic salts of the TTP^{4-} anion.*

Compd	NC[a]	OB[b]	H_L[c]	HOF[d]	HOF[d]	ρ[e]	VOD[f]	DP (GPa) [g]	T_{dec}[h]	Mp[i]
TTP	70.9	-91.1	--	1045	790	1.64	6.63	18.43	276	--
6.1	57.1	-136	3776	1035	421	1.48	5.20	10.58	263	153
6.2	51.0	-83.3	3587	1404	437	1.64	6.85	19.62	260	--
6.3	68.7	-103	3715	1985	728	1.56	6.40	16.60	249	129
6.4	66.2	-108	3831	1459	589	1.56	5.99	14.55	277	110
6.5	68.7	-103	3715	1383	507	1.56	5.98	14.49	282	95
6.6	70.8	-99	3613	1314	441	1.55	5.95	14.33	258	128
6.7	58.0	-62	3631	1919	594	1.71	7.53	24.41	226	212
6.8	62.6	-84	3641	1700	557	1.60	6.81	19.17	243	178
6.9	76.8	-78	3766	1964	715	1.64	6.84	19.58	265	--
6.10	68.3	-105	3453	1244	363	1.55	5.64	12.80	296	--
6.11	36.5	-65.2	3144	1786	348	1.70	7.51	24.13	260	190
6.12	71.0	-104	3859	322	139	1.49	5.23	10.76	180	--

[a] Nitrogen content (%). [b] Oxygen balance (%). [c] Lattice energy (kJmol^{-1}). [d] Heat of formation (kJmol^{-1}) (Calg^{-1}). [e] Density (gcm^{-3}). [f] Velocity of detonation (kms^{-1}). [g] Chapman-Jouguet detonation pressure (Gpa) [h] Thermal decomposition temperature under nitrogen gas (DSC-TGA, 10°C min^{-1}) (°C). [i] Melting point (°C).

6.3. Summary

In summary, a simple and straightforward approach for the synthesis of 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane (**TTP**) has been devised. Its salts, which can be easily synthesized and safely handled, exhibited promising physical properties, such as high nitrogen content, excellent thermal stabilities, and high positive heats of formation. The densities of these salts fell within the range 1.49–1.71 gcm^{-3}. The detonation velocities and detonation pressures of salts **6.7** and **6.11** were higher than that of TNT. All of the energetic salts examined herein showed moderate performance and high nitrogen content and, hence, may have potential applications in gas generators and pyrotechnics. Furthermore, this study is expected to provide some useful information for understanding the role of heterocycles and nitro and amino groups in the synthesis of energetic materials with improved properties.

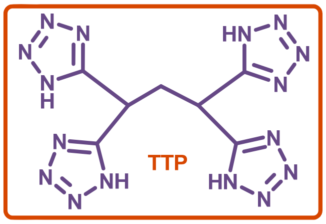
6.4 Experimental section

6.4.1. Materials and instrumentation

All reagents were commercially available and were used without further purification. Reactions were monitored by TLC analysis on pre-coated silica gel TLC plates (Merck). ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer with solvent as an internal standard [D6] DMSO d=2.5 ppm, tetramethylsilane (TMS) d=0.00 ppm). MS was performed on a LCMS spectrometer. Melting points and decomposition temperatures (DTA) were determined by differential scanning calorimetry thermogravimetric analysis (DSC-TGA). IR spectra were recorded on a Perkin–Elmer IR spectrometer by using KBr pellets. Elemental analysis was performed on a flash EA 1112 full automatic trace-element analyzer.

6.4.2. Synthetic Procedures

Synthesis of 1,1,3,3-Tetra(1H-tetrazol-5-yl)propane (TTP): TTP was synthesized using two different methods: (a) Sodium azide (0.202 g, 3.1 mmol) and iodine (0.240 g, 3.1 mmol) was added to a solution of propane-1,1,3,3-tetracarbonitrile (0.100 g, 0.69 mmol) in DMF (10 mL). The reaction mixture was refluxed for 6h with stirring. The reaction mixture was cooled to room temperature and added hydrochloric acid (10 mL, 1 M). The reaction mixture was extracted with ethyl acetate and dried over sodium sulfate. The solvent was removed under reduced pressure and the product was isolated with satisfactory purity as a white powder (0.160 g, 73.3 %). (b) TTP was earlier synthesized by Chafin et al. for multifunctional hydroxyethyl tetrazoles and similar method also tried for its synthesis [6]. The procedure is described as follows: To a mixture of 5.0 g propane-1,1,3,3-tetracarbonitrile (34.6 mmol) and 1.562 g zinc bromide (6.93 mmol) in 50 mL water was added 1.124 g sodium azide (17.3 mmol) and the solution heated to reflux. After stirring overnight the mixture was cooled and 10 mL concentrated HCl was added. The solids initially dissolved and a new solid precipitated after about 10 min. The mixture was stirred for an additional 50 min then the solids were filtered off and washed with water to give an orange solid. This could be recrystallized from 70 mL water (decolorizing carbon) to give 7.1 g of white crystals (63%). DSC-TGA (10 °C min^{-1}): 276 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3144, 3069, 2962, 2910, 2729, 2613, 2465, 1747, 1674, 1556, 1442, 1383, 1298, 1277, 1248, 1168, 1076, 1055.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 5.03 (t, 2H), 2.49 (t, 2H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 34.4, 30.0.

Mass : 317.

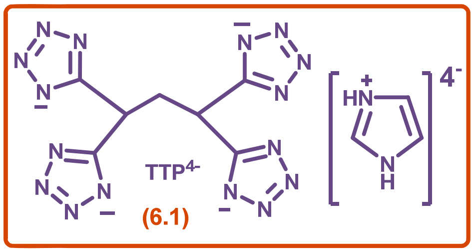
Anal. Calcd. for $C_7H_8N_{16}$: C, 26.59; H, 2.55; N, 70.86.

Found : C, 26.61; H, 2.51; N, 70.68.

General procedure for the preparation of TTP^{4-} Salts (6.1-6.12)

A solution of TTP (0.200 g, 0.632 mmol) in methanol (10 mL) was slowly added to a solution of cationic compound (2.53 mmol) in methanol (5 mL) at 25 °C with stirring. After stirring for 4h at room temperature, the solvent was removed in vacuo to leave the desired product.

***1H-Imidazol-3-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.1)*: Compound** **6.1** was prepared from imidazole (0.172 g, 2.53 mmol). White solid, 96.7% yield. DSC-TGA (10 °C min^{-1}): 153 °C (m.p.), 263 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3112, 2980, 1961, 1605, 1479, 1419, 1200, 1063, 953.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.37 (s, 8H), 7.35 (s, 4H) 4.75 (t, 2H), 3.15 (t, 2H).

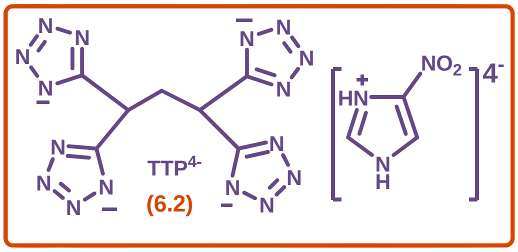
^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.7, 135.3, 121.0 36.8, 30.9.

Mass : 589.

Anal. Calcd. for $C_{19}H_{24}N_{24}$: C, 38.77; H, 4.11; N, 57.12.

Found : C, 38.65; H, 4.05; N, 57.32.

Tris(4-nitro-1H-imidazol-3-ium)-5-nitro-1H-imidazol-3-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.2)**:** Compound **6.2** was prepared from 4-nitroimidazole (0.286 g, 2.53 mmol). White solid, 96.6% yield. DSC-TGA (10 °C min^{-1}): 260 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3139, 3018, 2876, 1561(NO_2), 1506, 1429, 1385, 1330, 1248, 1078.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 13.24 (s, 4H), 8.32 (s, 4H), 7.85 (s, 4H) 5.05 (t, 2H), 3.29 (t, 2H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.6, 148.0, 136.3, 119.5, 34.5, 30.1.

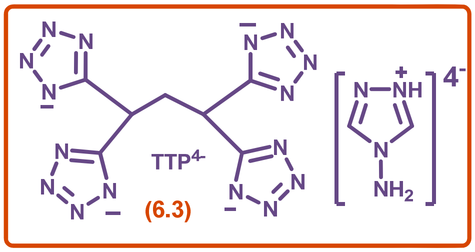
Mass : 769.

Anal. Calcd. for $C_{19}H_{20}N_{28}O_8$: C, 29.69; H, 2.62; N, 51.03.

Found : C, 29.76; H, 2.21; N, 51.15.

***4-Amino-4H-1,2,4-triazol-1-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.3)*:**

Compound 6.3 was prepared from 4*H*-1,2,4-triazol-4-amine (0.210 g, 2.53 mmol). White solid, 75.1% yield. DSC-TGA (10 °C min^{-1}): 129 °C (m.p.), 249 °C (dec).

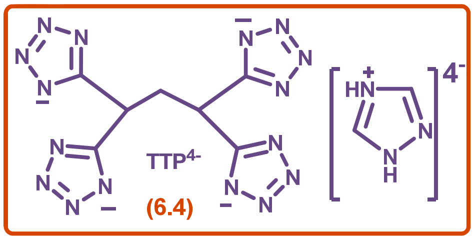


(6.3)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3321, 3130, 2721, 2607, 1640, 1552, 1433, 1381, 1246, 1195, 1065.
^{1}H NMR (400 MHz, DMSO)	: δ (ppm) 8.46 (s, 8H), 6.34 (s, 12H) 5.03 (t, 2H), 3.28 (t, 2H).
^{13}C NMR (100MHz, DMSO)	: δ (ppm) 156.7, 144.6, 34.6, 30.1.
Mass	: 653.
Anal. Calcd. for $C_{15}H_{24}N_{32}$	: C, 27.61; H, 3.71; N, 68.68.
Found	: C, 27.48; H, 3.65; N, 68.56.

***1H-1,2,4-Triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.4)*:**

Compound 6.4 was prepared from 1*H*-1,2,4-triazole (0.174 g, 2.53 mmol). White solid, 99% yield. DSC-TGA (10 °C min^{-1}): 110 °C (m.p.), 277 °C (dec).



(6.4)

IR (KBr pellet, ν_{max}/cm^{-1})	: 3124, 2865, 2694, 1762, 1685, 1555, 1488, 1446, 1379,

1265, 1250, 1151, 1053.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 10.97 (s, 4H), 8.31 (s, 8H) 5.08 (t, 2H), 3.33 (t, 2H).

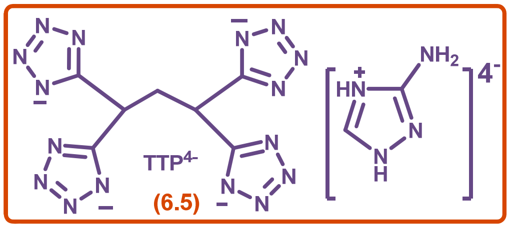
^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.6, 147.2, 34.6, 30.1.

Mass : 591.

Anal. Calcd. for $C_{15}H_{20}N_{28}$: C, 30.41; H, 3.40; N, 66.19.

Found : C, 30.56; H, 3.32; N, 66.31.

***3-Amino-1H-1,2,4-triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.5)*:** Compound **6.5** was prepared from 1*H*-1,2,4-triazol-3-amine (0.212 g, 2.53 mmol). White solid, 99.3% yield. DSC-TGA (10 °C min^{-1}): 95 °C (m.p.), 282 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3342, 3145, 2731, 1685, 1622, 1565, 1467, 1389, 1312, 1260, 1162, 1032.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 7.65 (s, 4H) 4.91 (t, 2H), 3.23 (t, 2H).

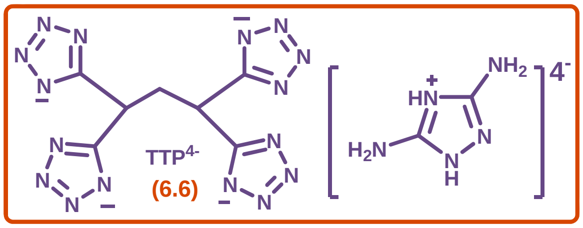
^{13}C NMR (100MHz, DMSO) : δ (ppm) 157.4, 156.9, 146.4, 49.0, 30.4.

Mass : 653.

Anal. Calcd. for $C_{15}H_{24}N_{32}$: C, 27.61; H, 3.71; N, 68.68.

Found : C, 27.45; H, 3.78; N, 68.51.

3,5-Diamino-1H-1,2,4-triazol-4-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetr-azol-1-ide (6.6)**:** Compound **6.6** was prepared from 1*H*-1,2,4-triazole-3,5-diamine (0.250 g, 2.53 mmol). White solid, 97.1% yield. DSC-TGA (10 °C min^{-1}): 128 °C (m.p.), 258 °C (dec.1), 305 (dec.2).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3363, 3301, 3130, 1666, 1624, 1552, 1484, 1407, 1345, 1055, 1008.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 6.51 (s, 16H), 4.72 (t, 2H), 3.09 (t, 2H).

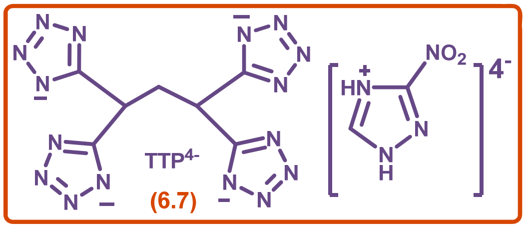
^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.1, 156.4, 49.1, 30.7.

Mass : 712.

Anal. Calcd. for $C_{15}H_{28}N_{36}$: C, 25.28; H, 3.96; N, 70.76.

Found : C, 25.31; H, 3.36; N, 71.25.

3-Nitro-1H-1,2,4-triazol-4-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.7)**:** Compound **6.7** was prepared from 3-nitro-1,2,4-triazole (0.288 g, 2.53 mmol). White solid, 98.2% yield. DSC-TGA (10 °C min^{-1}): 212 °C (m.p.), 226 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3156, 3040, 2964, 2871, 1561, 1517, 1479, 1424, 1375, 1304, 1260, 1172, 1101.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 8.86 (s, 4H), 5.03 (t, 2H), 2.49 (t, 2H).

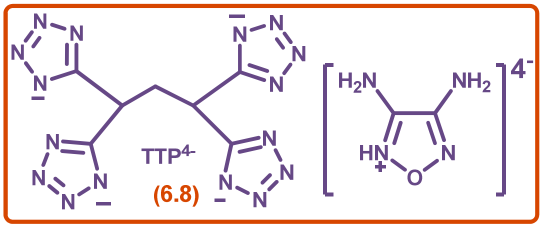
^{13}C NMR (100MHz, DMSO) : δ (ppm) 163.5, 156.6, 146.7, 34.5, 30.1.

Mass : 773.

Anal. Calcd. for $C_{15}H_{16}N_{32}O_8$: C, 23.32; H, 2.09; N, 58.02.

Found : C, 23.18; H, 2.16; N, 58.15.

3,4-Diamino-1,2,5-oxadiazol-2-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetra -zol-1-ide (6.8)**:** Compound **6.8** was prepared from 3,4-diaminofurazan (0.253 g, 2.53 mmol). White solid, 96.6% yield. DSC-TGA (10 °C min^{-1}): 178 °C (m.p.), 243 °C (dec.1), 273 (dec.2).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3424, 3314, 3144, 3062, 2964, 2920, 2881, 2717, 2618, 2459, 1643, 1555, 1440, 1341, 1243, 1073, 1051.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 5.81 (s, 1H), 5.06 (t, 2H), 3.31 (t, 2H).

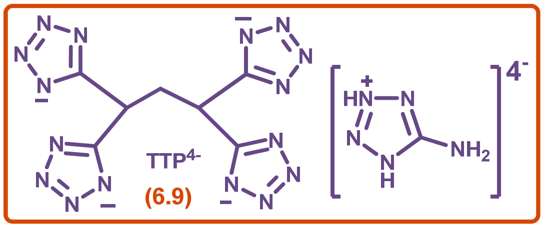
^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.5, 150.2, 34.5, 30.1.

Mass : 717.

Anal. Calcd. for $C_{15}H_{24}N_{32}O_4$: C, 25.14; H, 3.38; N, 62.55; O, 8.93.

Found : C, 25.12; H, 3.31; N, 62.36.

5-amino-1H-tetrazol-2-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.9)**:** Compound **6.9** was prepared from 1*H*-tetrazol-5-amine (0.215 g, 2.53 mmol). White solid, 99% yield. DSC-TGA (10 °C min^{-1}): 265 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3156, 3063, 2964, 2717, 1682, 1556, 1441, 1386, 1243, 1106, 1057, 1002.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 11.06 (s, 4H), 5.05 (t, 2H), 3.29 (t, 2H).

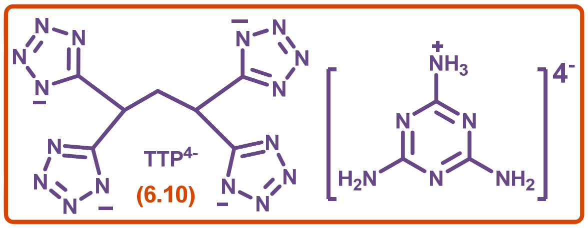
^{13}C NMR (100MHz, DMSO) : δ (ppm) 170.1, 156.6, 34.5, 30.1.

Mass : 657.

Anal. Calcd. for $C_{11}H_{20}N_{36}$: C, 20.12; H, 3.07; N, 76.81.

Found : C, 20.21; H, 3.12; N, 76.91.

4,6-Diamino-1,3,5-triazin-2-aminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)titrate-trazol-1-ide (6.10)**:** Compound **6.10** was prepared from 1,3,5-triazine-2,4,6-triamine (0.319 g, 2.53 mmol). White solid, 94.4% yield. DSC-TGA (10 °C min^{-1}): 296 °C (dec).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3419, 3331, 3101, 1665, 1610, 1545, 1495, 1402, 1183, 1123, 1019.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 7.090 (s, 12 H), 4.99 (s, 16H), 4.93 (t, 2H), 3.32 (t, 2H).

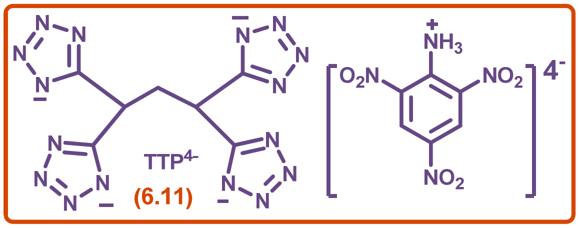
^{13}C NMR (100MHz, DMSO) : δ (ppm) 164.5, 158.5, 36.7, 30.9.

Mass : 819.

Anal. Calcd. for $C_{19}H_{32}N_{40}$: C, 27.81; H, 3.93; N, 68.26.

Found : C, 27.72; H, 3.85; N, 68.11.

2,4,6-Trinitrobenzenaminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.11)**:** Compound **6.11** was prepared from 2,4,6-trinitroaniline (0.576 g, 2.53 mmol). Yellow solid, 92.6% yield. DSC-TGA (10 °C min^{-1}): 190 °C (m.p.), 260 °C (dec.1), 280 (dec.2).



(6.11)

IR (KBr pellet, ν_{max}/cm^{-1}) : 3430, 3314, 3079, 1632, 1583, 1528, 1419, 1271, 1156, 1079, 1041.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 9.06 (s, 8H), 8.99 (s, 12H), 5.04 (t, 2H), 3.29 (t, 2H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 156.6, 144.0, 134.7, 133.1, 128.5, 34.5, 30.1.

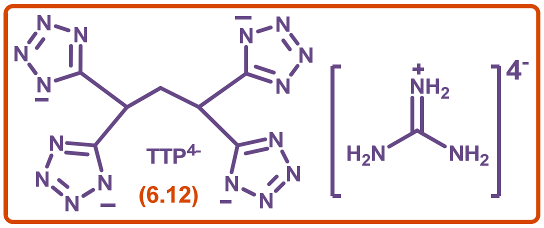
Mass : 1228.

Anal. Calcd. for $C_{31}H_{24}N_{32}O_{24}$: C, 30.30; H, 1.97; N, 36.48; O, 31.25.

Found : C, 30.21; H, 1.91; N, 36.52.

Diaminomethaniminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (6.12):

Compound **6.12** was prepared from guanidine (0.309 g, 2.53 mmol). White solid, 94.4% yield. DSC-TGA (10 °C min^{-1}): 180 °C (dec.1), 270 (dec.2).



IR (KBr pellet, ν_{max}/cm^{-1}) : 3369, 3199, 3062, 2739, 1671, 1561, 1364, 1243, 1084, 1057.

^{1}H NMR (400 MHz, DMSO) : δ (ppm) 6.98 (s, 16H) 5.04 (t, 2H), 3.28 (t, 2H).

^{13}C NMR (100MHz, DMSO) : δ (ppm) 158.4, 156.5, 34.5, 30.0.

Mass : 553.

Anal. Calcd. for $C_{11}H_{28}N_{28}$: C, 23.91; H, 5.11; N, 70.98.

Found : C, 23.81 5.21; N, 70.85.

6.5. References

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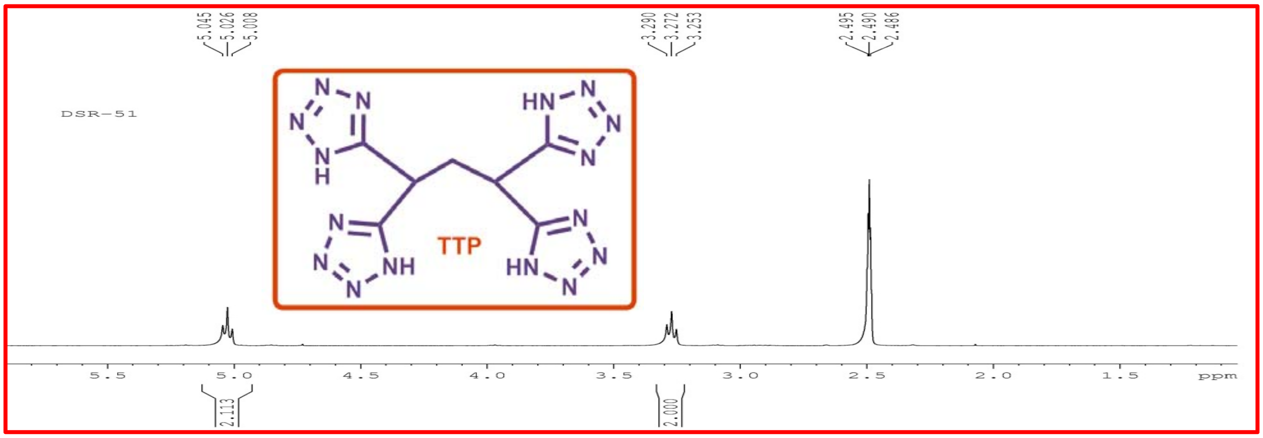


Figure 2.S1 *^{1}H NMR spectrum of 1,1,3,3-Tetra(1H-tetrazol-5-yl)propane (**TTP**)*

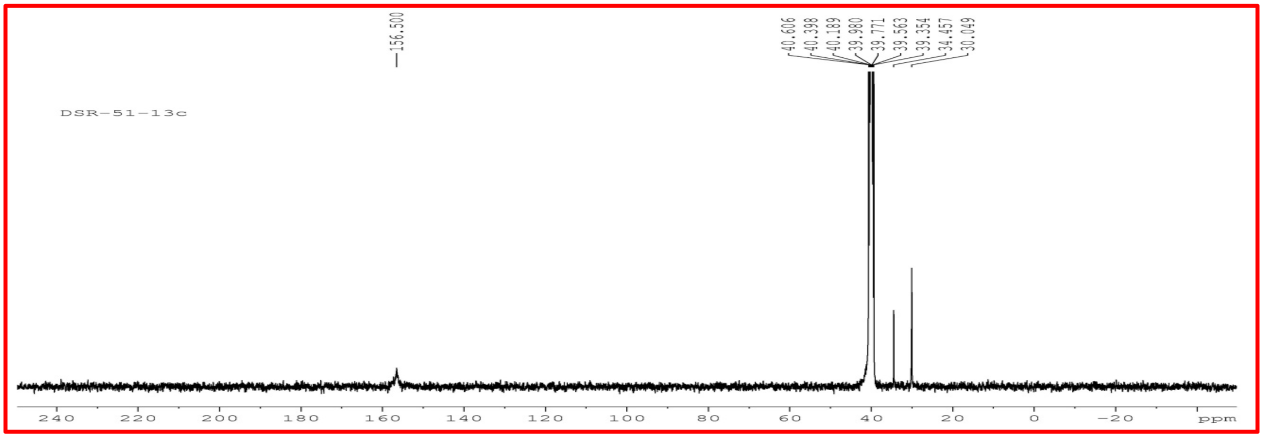


Figure 2.S2 *^{13}C NMR spectrum of 1,1,3,3-Tetra(1H-tetrazol-5-yl)propane (**TTP**)*

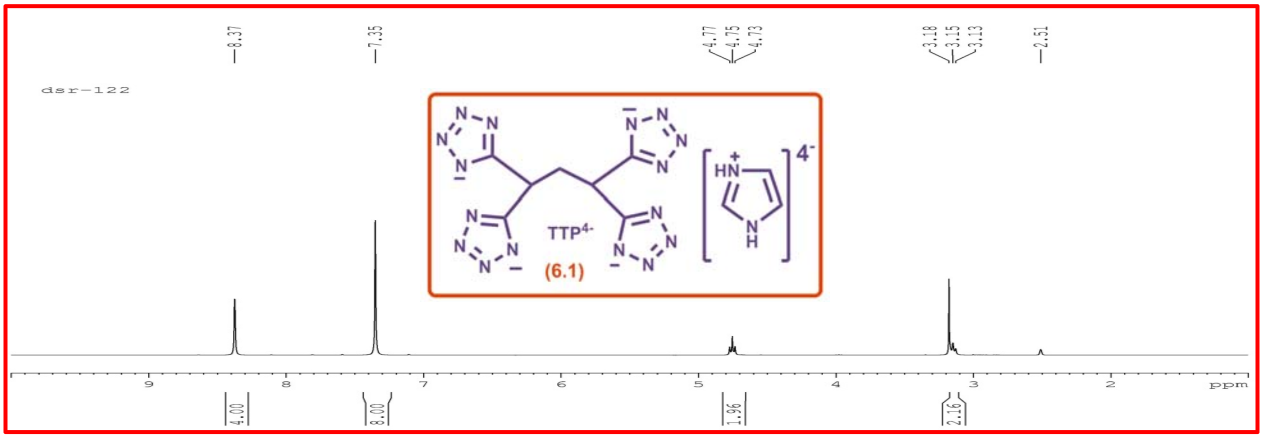


Figure 2.S3 *^{1}H NMR spectrum of 1H-imidazol-3-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide (**6.1**)*

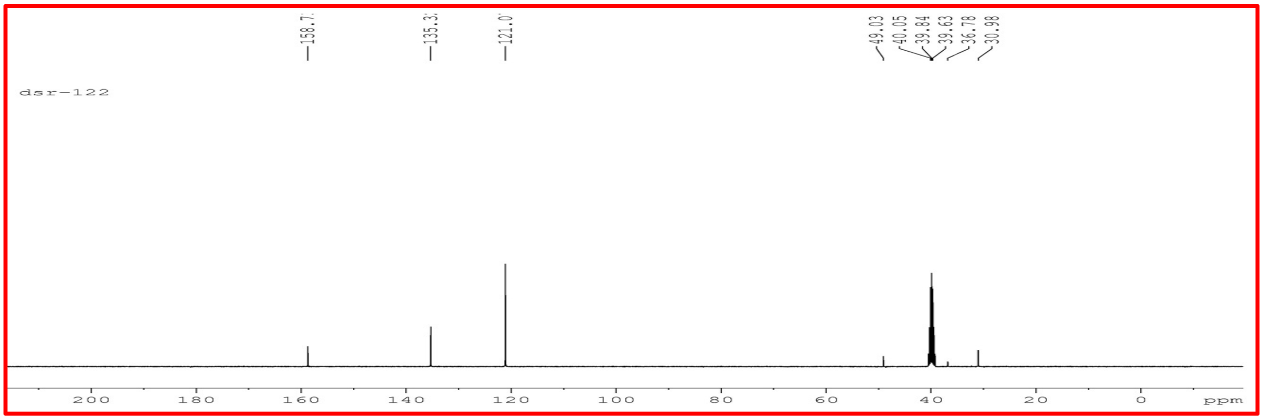


Figure 2.S4 ^{13}C NMR spectrum of 1H-imidazol-3-ium 5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.1)**

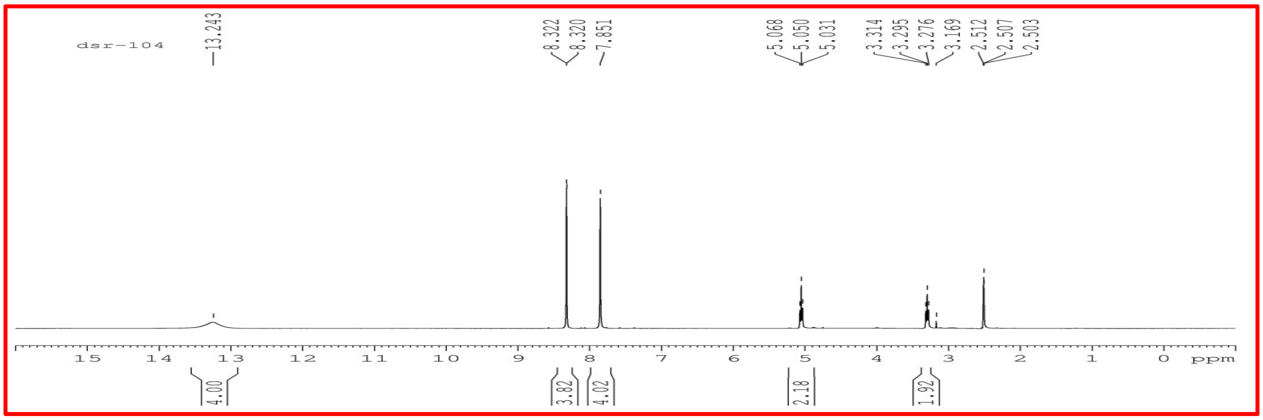


Figure 2.S5 ^{1}H NMR spectrum of Tris(4-nitro-1H-imidazol-3-ium)-5-nitro-1H-imidazol-3-ium-5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.2)**

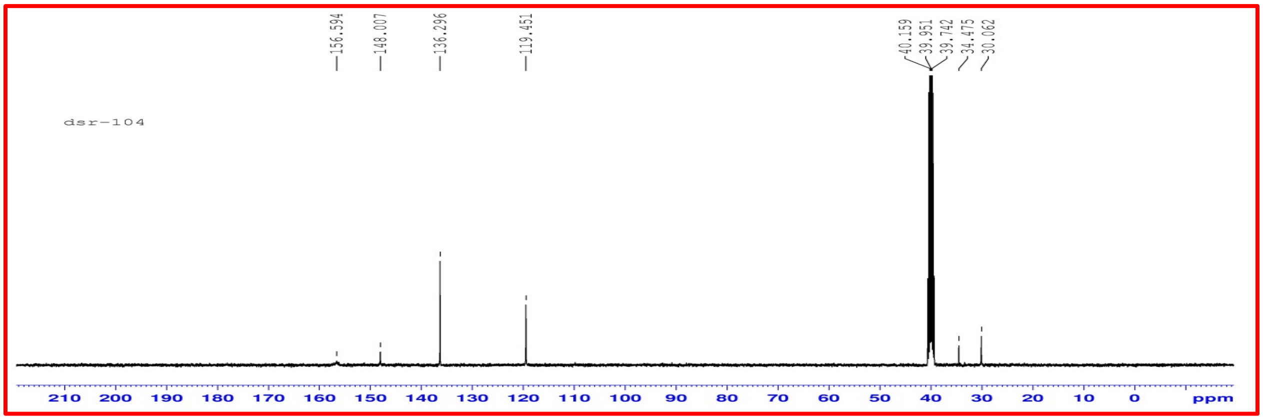


Figure 2.S6 ^{13}C NMR spectrum of Tris(4-nitro-1H-imidazol-3-ium)-5-nitro-1H-imidazol-3-ium-5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.2)**

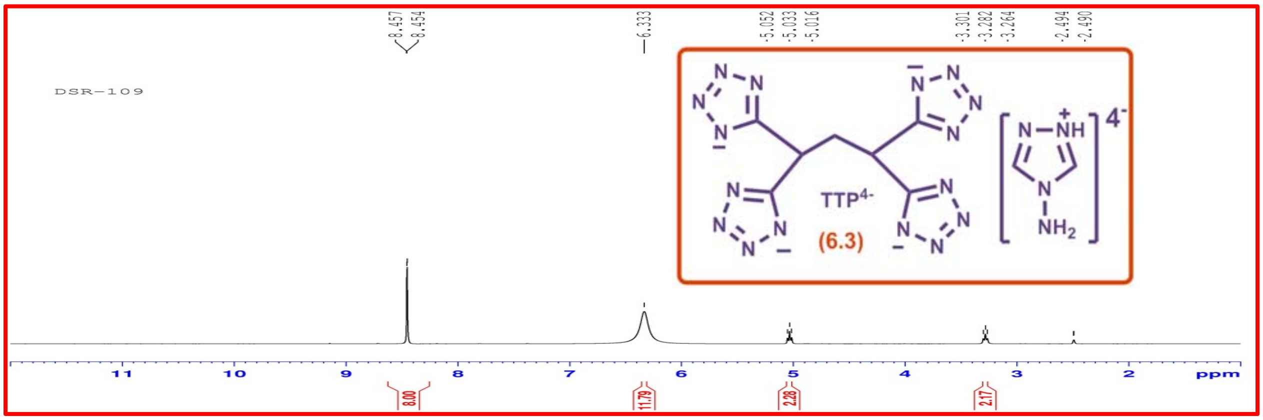


Figure 2.S7 ^{1}H NMR spectrum of 4H-1,2,4-Triazol-1-aminium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.3)**

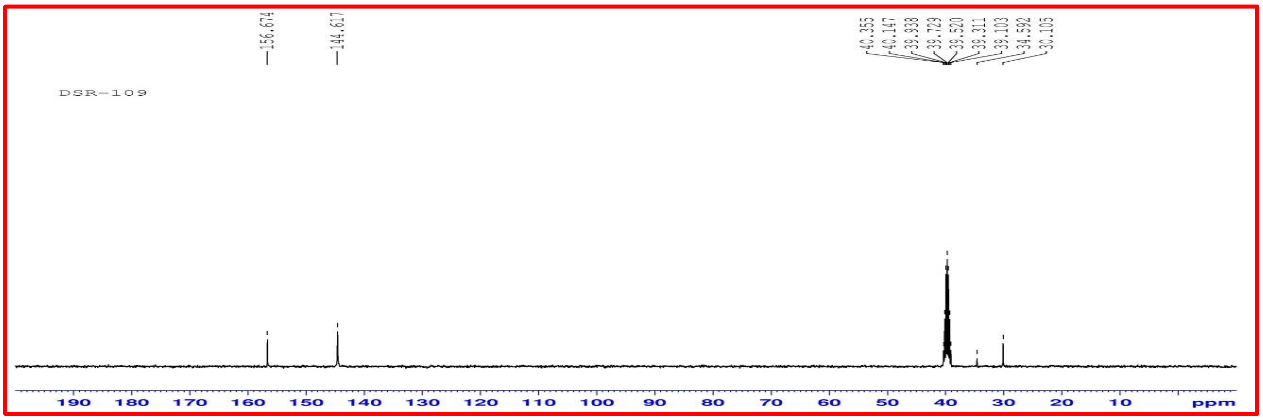


Figure 2.S8 ^{13}C NMR spectrum of 4H-1,2,4-Triazol-1-aminium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.3)**

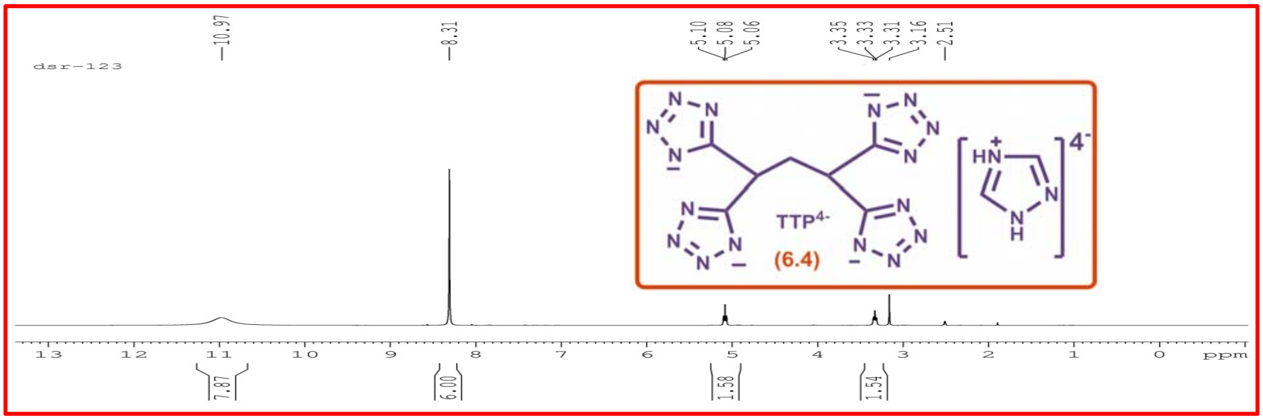


Figure 2.S9 ^{1}H NMR spectrum of 1H-1,2,4-triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.4)**

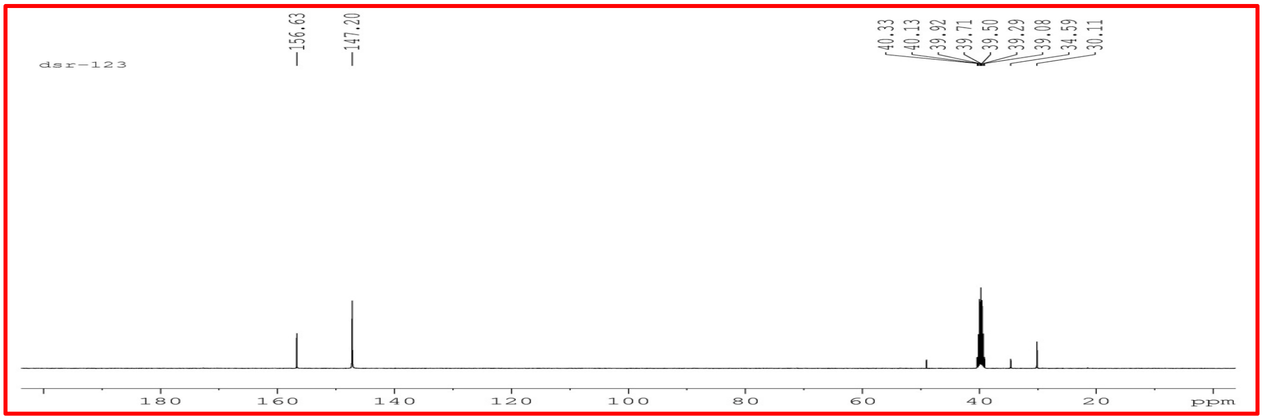


Figure 2.S10 ^{13}C *NMR spectrum of 1H-1,2,4-triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* *(6.4)*

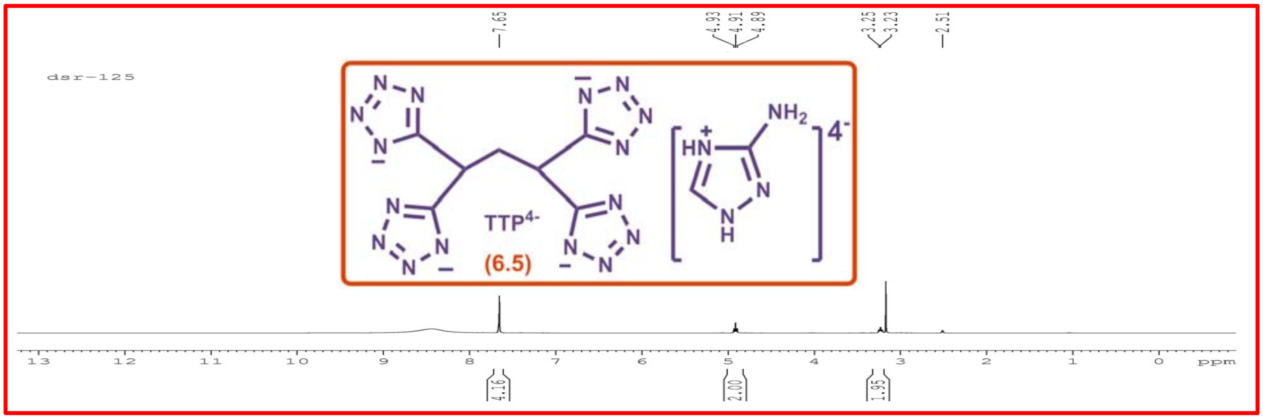


Figure 2.S11 ^{1}H *NMR spectrum of 3-amino-1H-1,2,4-triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* *(6.5)*

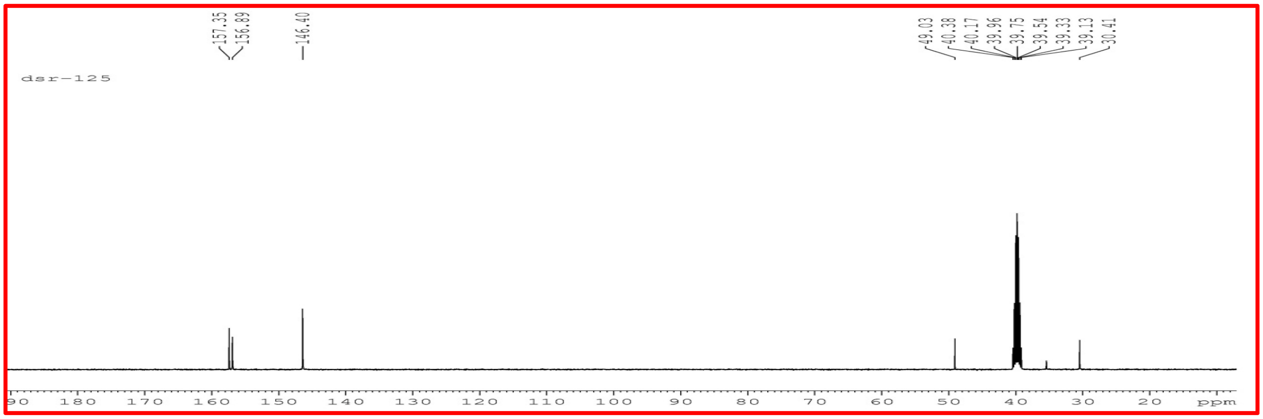


Figure 2.S12 ^{13}C *NMR spectrum of 3-amino-1H-1,2,4-triazol-4-ium 5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* *(6.5)*

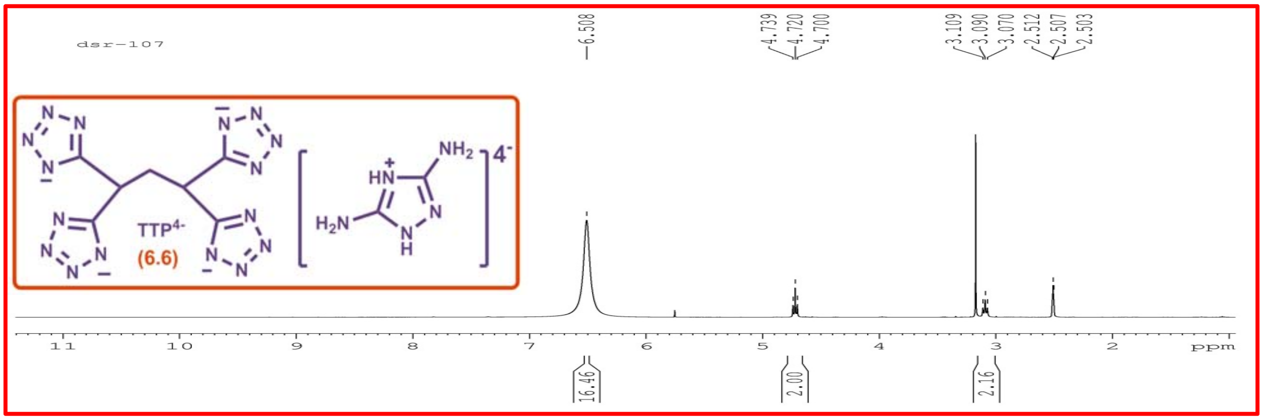


Figure 2.S13 *^{1}H NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.6)***

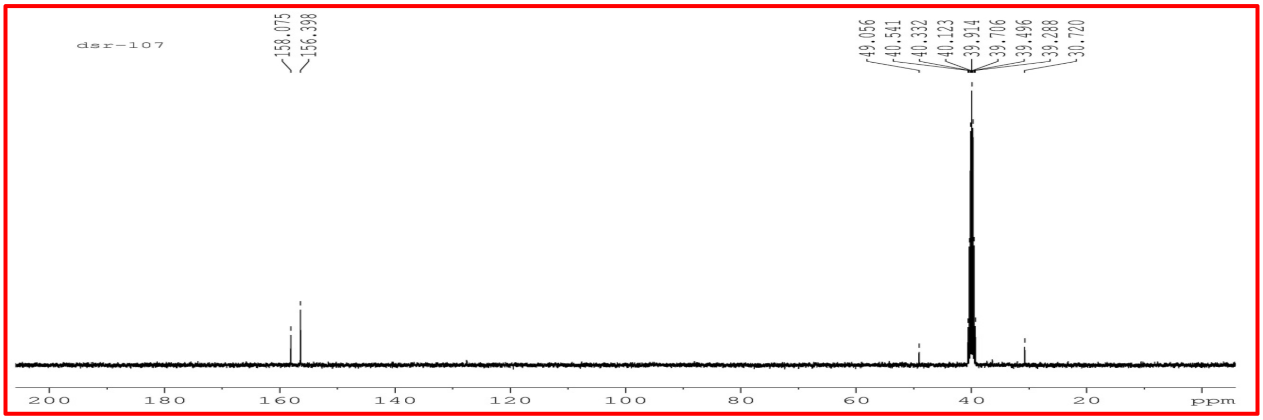


Figure 2.S14 *^{13}C NMR spectrum of 3,5-Diamino-1H-1,2,4-triazol-4-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.6)***

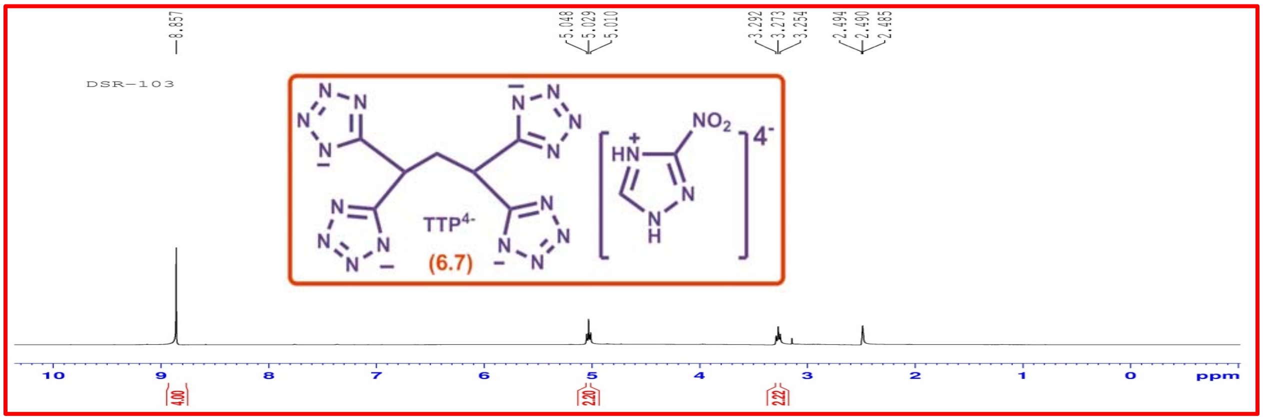


Figure 2.S15 *^{1}H NMR spectrum of 3-Nitro-1H-1,2,4-triazol-4-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.7)***

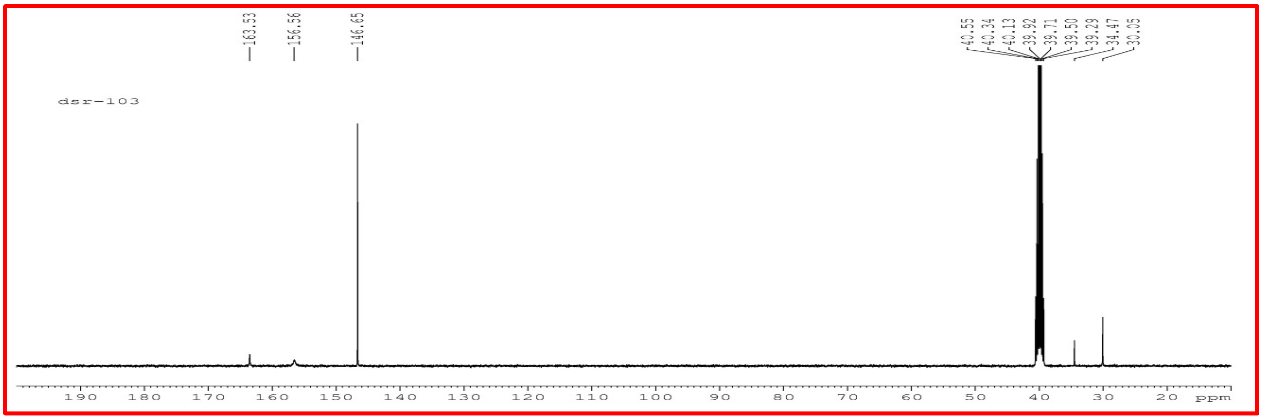


Figure 2.S16 ^{13}*C NMR spectrum of 3-Nitro-1H-1,2,4-triazol-4-ium5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* *(6.7)*

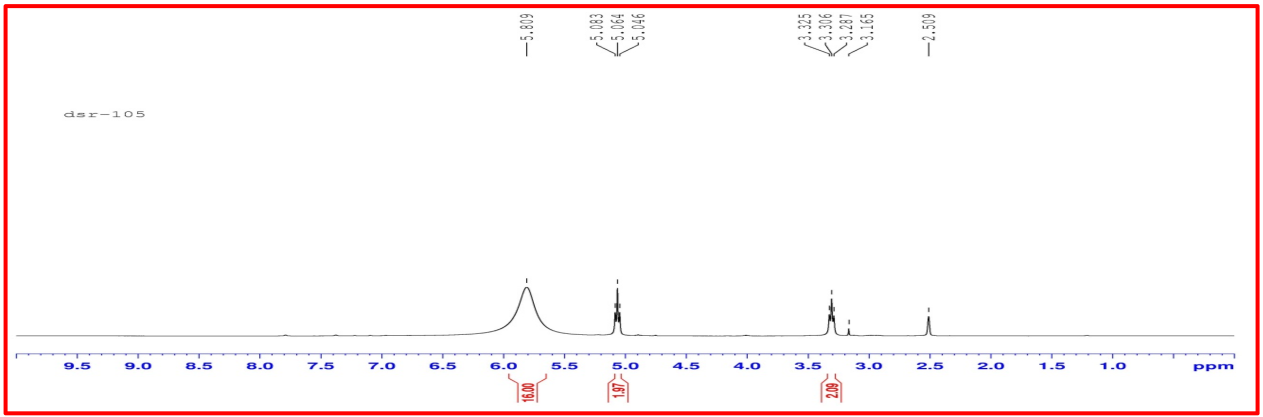


Figure 2.S17 ^{1}*H NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetra -zol-1-ide* *(6.8)*

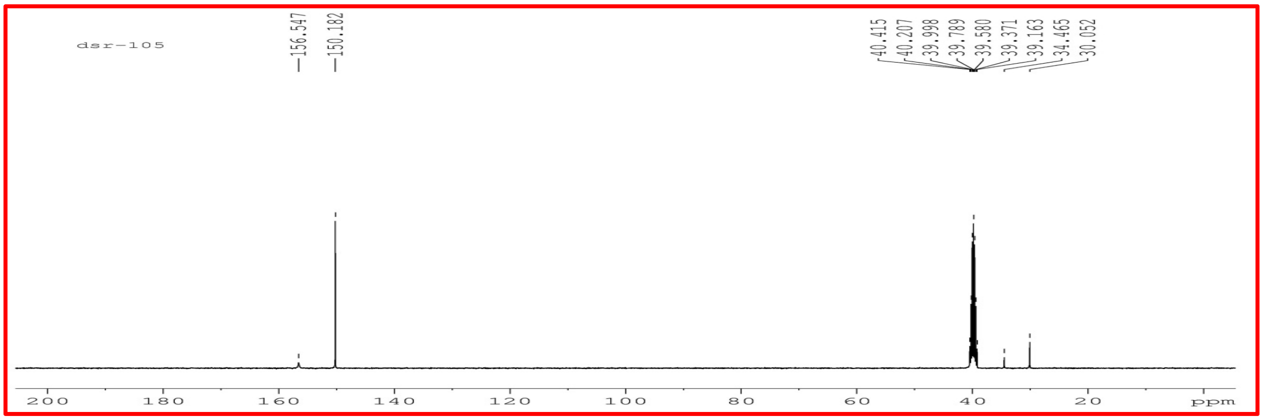


Figure 2.S18 ^{13}*C NMR spectrum of 3,4-Diamino-1,2,5-oxadiazol-2-ium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetra -zol-1-ide* *(6.8)*

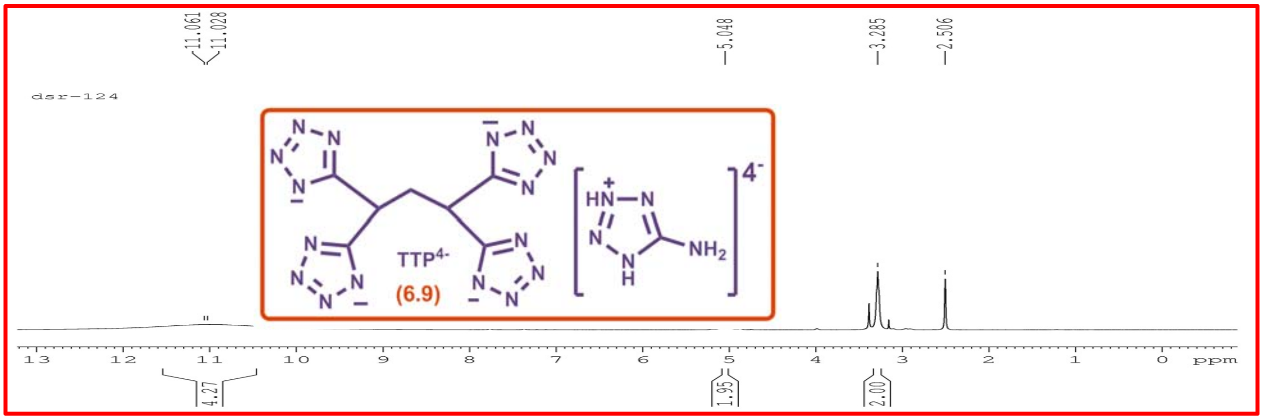


Figure 2.S19 *^{1}H NMR spectrum of 5-amino-1H-tetrazol-2-ium5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.9)***

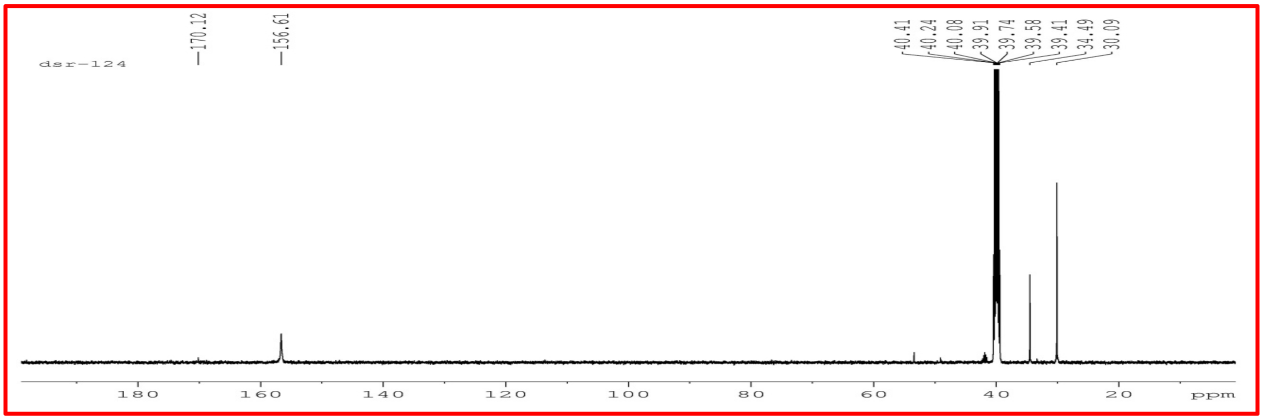


Figure 2.S20 *^{13}C NMR spectrum of 5-amino-1H-tetrazol-2-ium5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.9)***

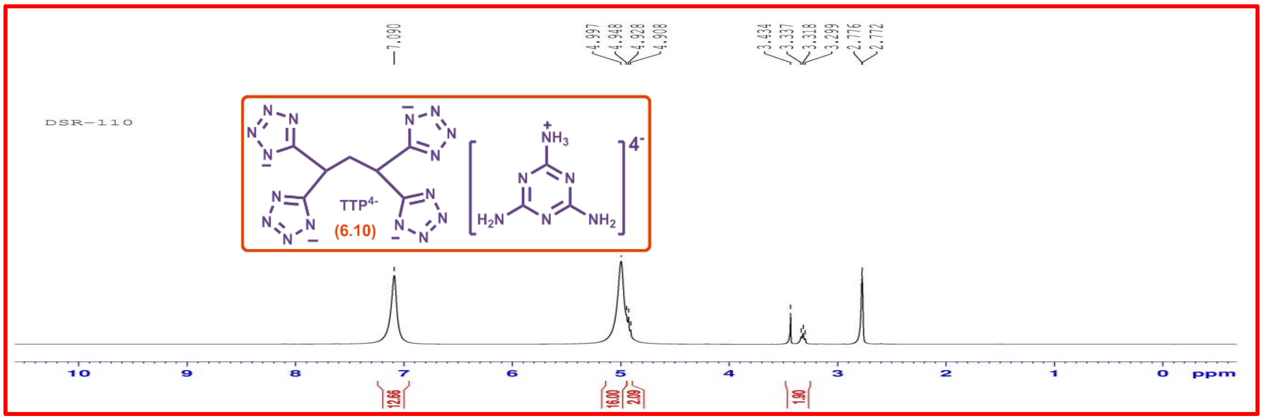


Figure 2.S21 *^{1}H NMR spectrum of 4,6-Diamino-1,3,5-triazin-2-aminium-5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)titratetra zol-1-ide* ***(6.10)***

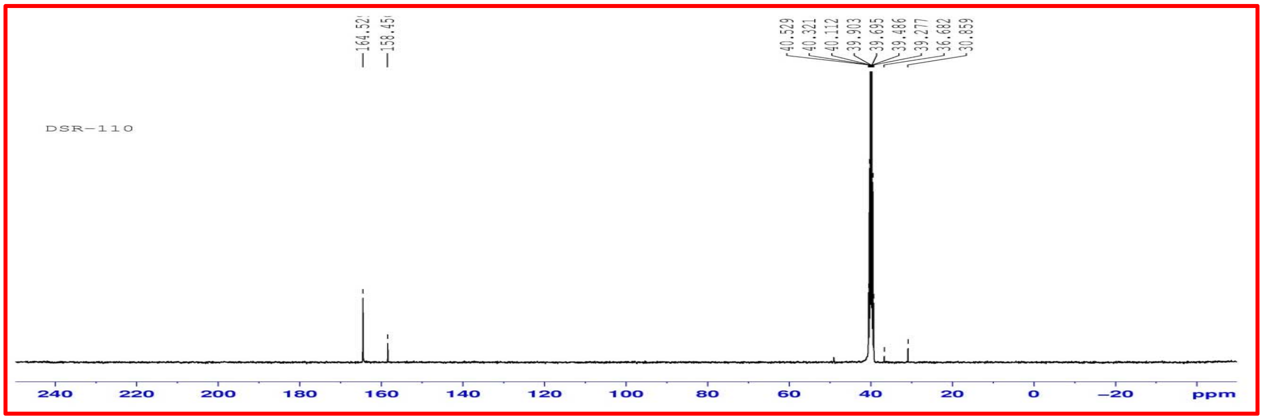


Figure 2.S22 *^{13}C NMR spectrum of 4,6-Diamino-1,3,5-triazin-2-aminium-5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)titratetra zol-1-ide* ***(6.10)***

Figure 2.S23 *^{1}H NMR spectrum of 2,4,6-Trinitrobenzenaminium 5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.11)***

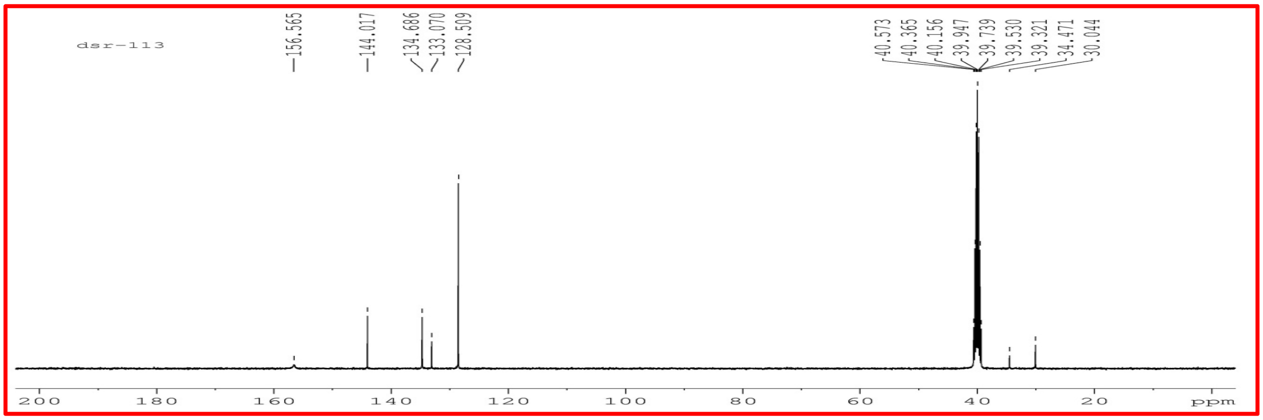


Figure 2.S24 *^{13}C NMR spectrum of 2,4,6-Trinitrobenzenaminium 5,5′,5″,5‴-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.11)***

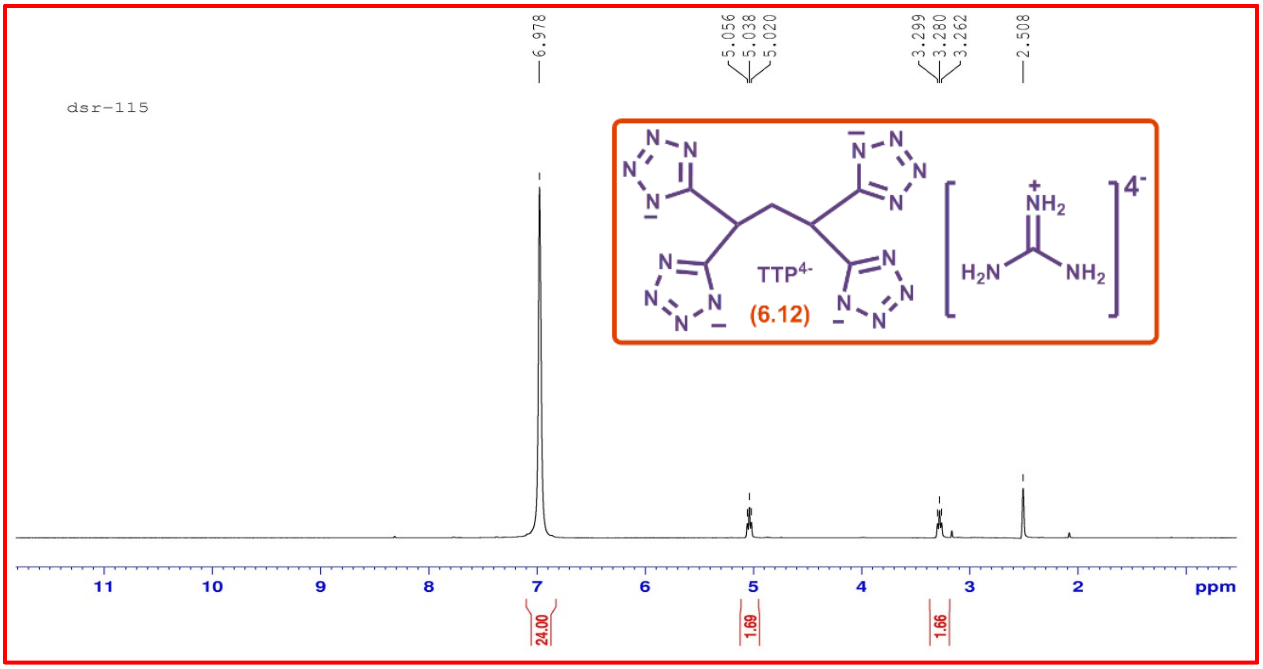


Figure 2.S25 ^{1}H NMR spectrum of Diaminomethaniminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide **(6.12)**

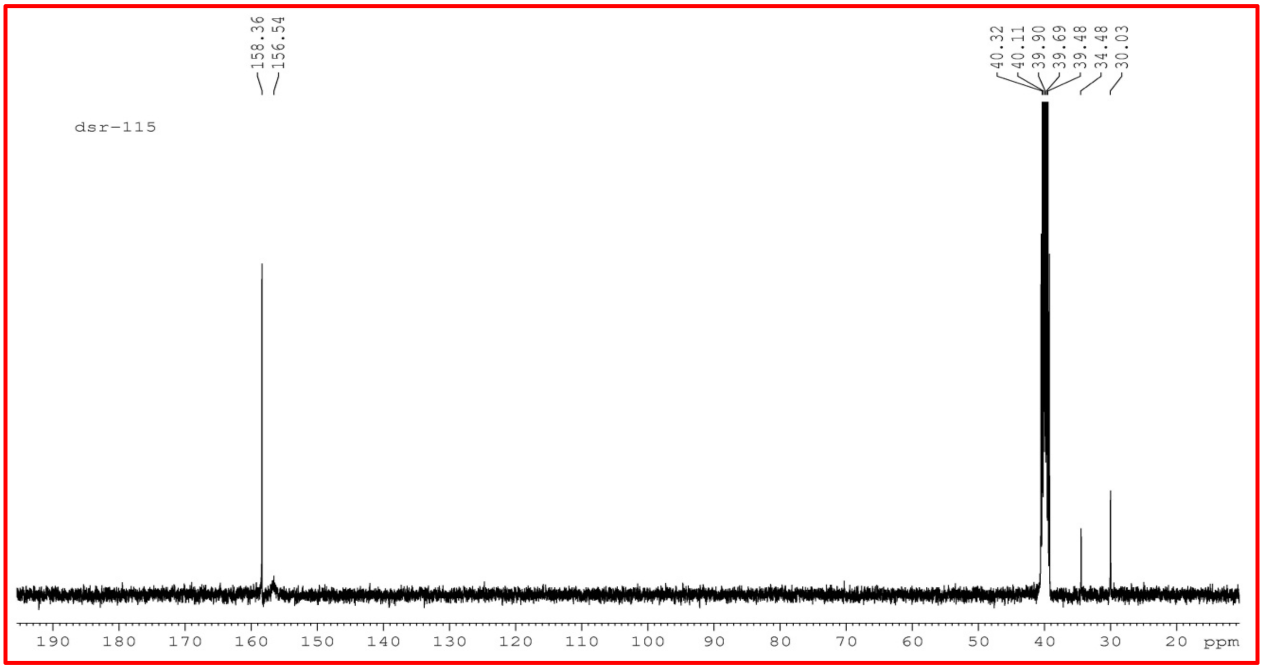


Figure 2.S26 *^{13}C NMR spectrum of Diaminomethaniminium-5,5',5'',5'''-(propane-1,1,3,3-tetrayl)tetratetrazol-1-ide* ***(6.12)***

Annexure-I

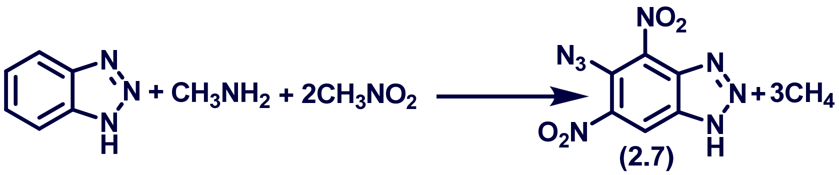
A. Introduction:

The major research in the energetic materials field is focused on the development of new compounds with higher performance and enhanced insensitivity than the existing ones in order to meet the requirements of future military and space applications [1]. In other words, one can say that higher performance and enhanced insensitivity decide the fate of newly developed materials. Thus, in modern ordnance there are strong requirements for energetic materials having good thermal stability, impact & shock insensitivity and better performance. However, these requirements are somewhat mutually elite. The materials having good thermal stability and impact insensitivity usually exhibit poorer performance and vice versa. Therefore, the foremost objective at this stage is the screening of hypothetical energetic materials through computational modeling, which allow experimental researchers to expend resources only on those molecules that show promise of enhanced performance, reduced sensitivity, or reduced environmental hazards. Computational modeling is an eminent tool for both theoreticians and experimentalists in analyzing the chemistry related problems. The ability to design new materials from quantum mechanical principles with computers is currently one of the fastest growing and most exciting areas of theoretical research. The high costs and time associated with the synthesis or formulation, testing and fielding of a new energetic material have called for the inclusion of modeling and simulation into the energetic materials design process. This has resulted in growing demands for accurate models to predict the properties and behavior of notional energetic materials before committing resources for their development. Development of predictive models that will allow for the screening and elimination of poor candidates before the expenditure of time and resources for synthesis and testing of advanced materials is the major goal to include computational methodology in this work. This expected to give economic benefit in the development of a new material.

The development of accurate models and simulations of explosives has been aggressively pursued within the energetic material research since the arrival of computational capabilities. Of particular importance in designing new explosives, is the ability to predict performance of compounds before the laborious and expensive task of synthesizing them. The significant key properties of energetic materials are heat of formation, density and detonation performance. All computations were performed with Gaussian 03 package at B3LYP and B3PW91 hybrid method with 6-31G(d,p) basis set. The structural parameters were allowed to be optimized and no constraints were imposed on molecular structure during the optimization process. All optimized structures were characterized to the true local energy minima on potential energy surfaces without imaginary frequencies.

B. Heat of formation:

Heat of formation is a measure of energy content of an energetic material that can decompose, ignite and explode by heat or impact. However, it is impractical to determine the heat of formation of novel energetic materials because of their unstable intermediates and unknown combustion mechanism. There are various methods known for the calculation of heat of formation such as, Group additivity method, Atomization reactions, Linear regression correction approach, Bond correction terms, Homodesmic reactions, and Isodesmic reaction approach [2]. Group additivity method, Atomization reactions, Linear regression correction approach, and Bond correction terms are not widely used as they are not suitable for isomers. In the homodesmic reaction, numbers of bonds of various types are conserved along with preservation of valence environment around each atom. Therefore, for various reference compounds experimental data is not available in homodesmic reactions. In recent studies, the isodesmic reaction approach is widely used, in which the number of each kind of formal bond is conserved, is used with an application of the bond separation reaction (BSR) rules [3]. For example, the isodesmic reaction for compounds 2.7, 3.7, DNP, 5.2 and TTP is shown in Figure 1. In general, the use of an isodesmic reaction scheme leads to more effective cancellation of errors in computing enthalpies of reaction than atomization reactions or group additivity methods.



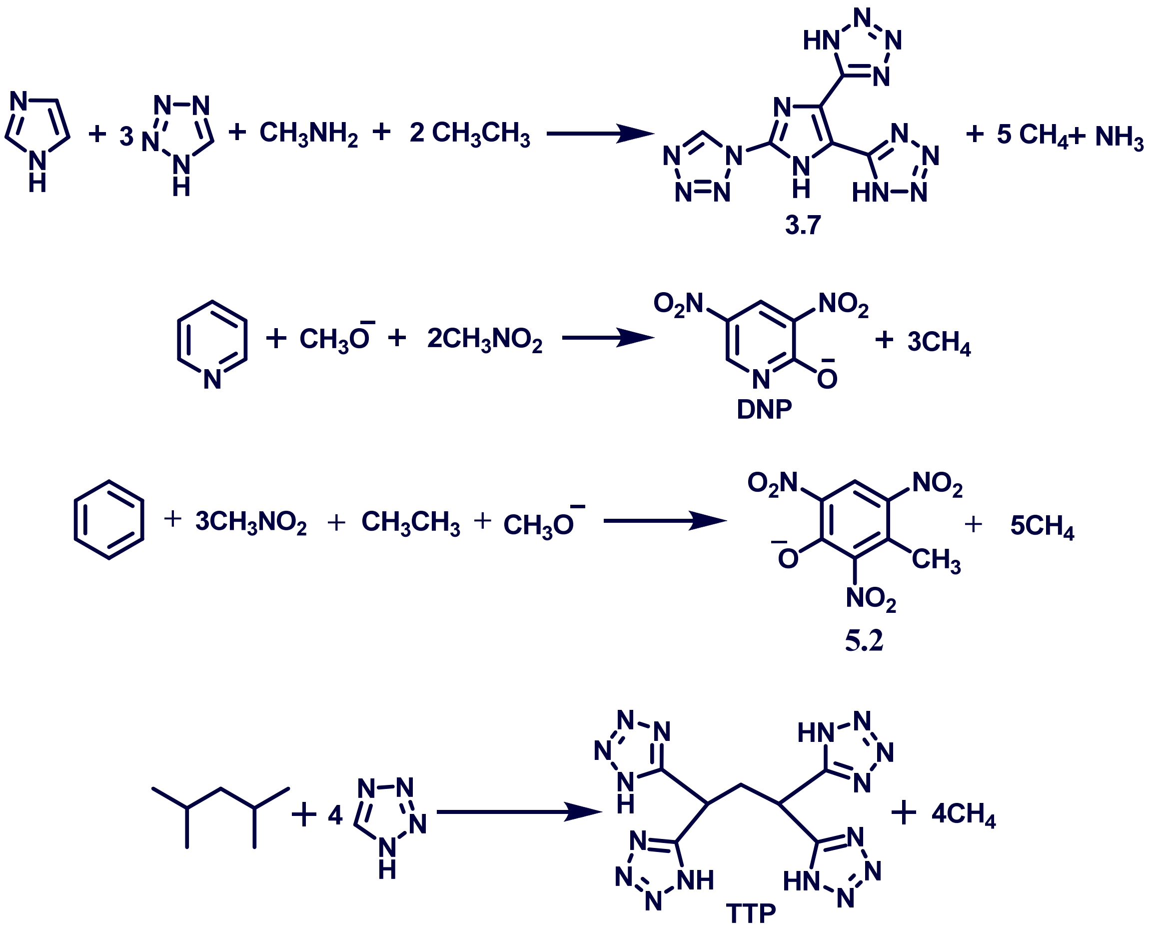


Figure 1. *Isodesmic reaction schemes for some of the selected compounds.*

Errors in the absolute quantities from quantum chemical calculations are often systematic and these errors can be compensated by employing isodesmic reactions. Previous studies also prove that this approach is reliable. For the isodesmic reaction, heat of reaction $\Delta H_{298\mathrm{K}}$ at 298 K can be calculated from the following equation (1):

$$\Delta H_{298\mathrm{K}} = \Delta H_{\mathrm{f,\,p}} - \Delta H_{\mathrm{f,\,R}} \qquad (1)$$

Where, $\Delta H_{\mathrm{f,\,R}}$ and $\Delta H_{\mathrm{f,\,p}}$ are the heats of formation of reactants and products at 298 K, respectively. The heat of formation of the designed molecules can be evaluated when the heat of reaction $\Delta H_{298\mathrm{K}}$ is known. Therefore, the principle thing is to compute the $\Delta H_{298\mathrm{K}}$. $\Delta H_{298\mathrm{K}}$ can be calculated using the following expression:

$$\Delta H_{298\mathrm{K}} = \Delta E_{298\mathrm{K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_{\mathrm{T}} + \Delta nRT \qquad (2)$$

where, ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE is the difference between the zero point energies (ZPE) of the products and the reactants, and ΔH_T is the thermal correction from 0 to 298 K. $\Delta(PV)$ the equals to ΔnRT for the reactions of ideal gas. Among the various approaches for the prediction of heat of formation, researchers in the energetic molecules field are widely using the isodesmic reaction approach due to the reliability and ease of use. The isodesmic reaction approach is proven to be simple and reliable method for the prediction of heats of formation for various types of compounds and hence, the gas phase heats of formation in the future study may be calculated using isodesmic approach. Politzer and coworkers [4] found that the heats of sublimation can correlate well with the molecular surface area and electrostatic interaction index $v\sigma^2_{tot}$ of energetic compounds. The electrostatic potential V(r) that is produced in the surrounding space around a molecule by its nuclei and electrons is given by following equation:

$$V(\mathrm{r}) = \sum_{A} \frac{Z_A}{|R_A - \mathrm{r}|} - \int \frac{\rho(\mathrm{r}')d\mathrm{r}'}{|\mathrm{r}' - \mathrm{r}|} \tag{3}$$

In above equation, Z_A is the charge on nucleus A, located at R_A, and $\rho(\mathrm{r})$ is the electronic density. V(r) is a physical observable, which can be determined experimentally by diffraction methods as well as computationally. The sign and magnitude of V(r) at any point **r** are the net result of the positive and negative contributions of the nuclei and the electrons, respectively. V(r) is commonly computed on an appropriate outer surface of the molecule and following the suggestion of Bader et al [5]. The 0.001 au (electrons/bohr^3) contour of the molecule's electronic density is frequently taken to be the surface. The positive and negative extrema are just two of several quantities that help to characterize the detailed features of the electrostatic potential on a molecular surface. The calculated electrostatic potential on this surface is characterized in terms of its average deviation Π and its total variances σ^2_{tot}; these are defined by equations (4 and 5):

$$\Pi = \frac{1}{t}\sum_{i=1}^{t} |V_s(r_i) - \overline{V}_s| \tag{4}$$

$$\sigma^2_{tot} = \sigma^2_+ + \sigma^2_- = \frac{1}{m}\sum_{j=1}^{m}[V_s^+(r_j) - \overline{V}_s^+]^2 + \frac{1}{n}\sum_{k=1}^{n}[V_s^-(r_k) - \overline{V}_s^-]^2 \tag{5}$$

$V(r_i)$ is the value of $V(r)$ at any point r_i on the surface, and $\overline{V}_s$ is the average over the entire surface. The variances σ_+^2, σ_-^2 and σ_{tot}^2 reflect the strengths and variabilities of the positive, negative and overall surface potentials. Due to the terms being squared, they emphasize particularly the local extrema, the $V_{S,max}$ and $V_{S,min}$ (there may be several of each). Finally, the parameter *v* is a measure of the degree of balance between the positive and negative potentials; when $\sigma_+^2 = \sigma_-^2$, *v* has its maximum value of 0.25. In these summations, t is the total number of points on the surface grid and m and n are the numbers of points at which $V_S(r)$ is positive, $V_s^+(r_j)$ and negative, $V_s^-(r_k)$, respectively. $\overline{V}_s, \overline{V}_s^+, \overline{V}_s^-$ and *v* (electrostatic balance parameter) are computed by appropriate summations over a finely spaced grid covering the entire molecular surface and defined in following equations (6-9):

$$\overline{V}_s = \frac{1}{t}\sum_{i=1}^{t} V_s(r_i) \tag{6}$$

$$\overline{V}_s^+ = \frac{1}{m}\sum_{j=1}^{m} V_s^+(r_j) \tag{7}$$

$$\overline{V}_s^- = \frac{1}{n}\sum_{k=1}^{n} V_s^-(r_k) \tag{8}$$

$$v = \frac{\sigma_+^2 \sigma_-^2}{(\sigma_+^2 + \sigma_-^2)^2} \tag{9}$$

For estimation of the potential performance of the energetic material, it is also significant to calculate their solid phase HOF (HOF_{Solid}) because it is related directly with the detonation characteristics. According to Hess' law, solid phase HOF can be obtained by,

$$HOF_{Solid} = HOF_{Gas} - HOF_{Sub} \tag{10}$$

Where HOF_{Sub} is the heat of sublimation and can be evaluated by the Byrd and Rice method [6] in the framework of the Politzer approach, using the following empirical relation,

$$\mathrm{HOF}_{Sub} = \beta_1 \mathrm{A}^2 + \beta_2 (v\sigma_{tot}^2)^{0.5} + \beta_3 \tag{11}$$

Where A is the area of the isosurface of 0.001 electrons/bohr^3 electronic density, v indicates the degree of balance between the positive and negative surface potentials, σ_{tot}^2 is a measure of variability of the electrostatic potential and β_1, β_2, and β_3 are determined through a least-squares with the experimental HOF_{Solid} of a selected set of known materials. Surface area, degree of balance between the positive and negative surface potentials and variability of the electrostatic potential are calculated using wave function analysis.

Heat of formation for energetic salts is predicted using the Born–Haber cycle. Based on the Born–Haber cycle (shown in Figure 2), the heat of formation of an ionic compound can be simplified by subtracting the lattice energy of the salt (H_L) from the total heat of formation of salt *i.e.* sum of the heats of formation of the cation and anion as shown in equation (12).

$$\mathrm{HOF\ (salt,\ 298\ K) = HOF\ (cation,\ 298\ K) + HOF\ (anion,\ 298\ K) - H_L} \tag{12}$$

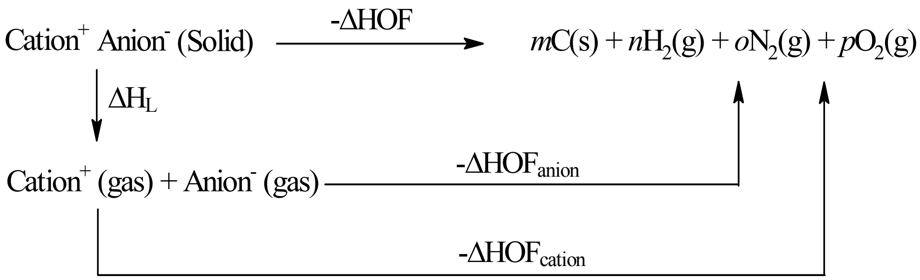


Figure 2. Born-Haber cycle for the formation of energetic salts.

Lattice potential energy is the energy associated with the process in which a crystalline solid lattice, M_pX_q is converted into its constituent gaseous ions, ${}_pM^{q+}$ (g) and ${}_qX^{p-}$ (g). The lattice energy can be predicted with reasonable accuracy by using Jenkins' equation (13) [7].

$$\mathrm{H_L} = U_{\mathrm{POT}} + [p(\frac{n_M}{2} - 2) + q(\frac{n_X}{2} - 2)]RT \tag{13}$$

Where *nM* and *nX* depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. When lattice potential energy (U_{POT}), is incorporated and made part of a Born–Haber cycle, it needs to be converted into a lattice enthalpy term. This lattice enthalpy (H_L), involves correction of the U_{POT} term by an appropriate number of RT terms. The U_{POT} ($kJmol^{-1}$) can be predicted from four different equations (14-17) as suggested by Jenkins et al [8]. Using following equations,

$$U_{POT} = AI(\tfrac{2I}{V})^{1/3} \tag{14}$$

$$U_{POT} = B(I^4 \tfrac{\rho}{M})^{1/3} \tag{15}$$

$$U_{POT} = \gamma(\tfrac{\rho}{M})^{1/3} + \delta \tag{16}$$

$$U_{POT} = 2I[\alpha(V)^{-1/3} + \beta] \tag{17}$$

In above equations (14-17), I is the ionic strength factor, where $I = {}^1/_2\Sigma n_i z_i^2$. Here n_i is the number of ions in the formula unit having a charge z_i. For the salts with 3:1 charge ratio (cation:anion) listed in this work, the ionic strength, I=6. ρ is the density (gcm^{-3}), V is the estimated volume of ionic material (nm^3) and M is the chemical formula mass of the ionic material ($gmol^{-1}$). The coefficients A (121.4 $kJmol^{-1}$), B (1291.7 $kJmol^{-1}$), γ (2342.6·I $kJmol^{-1}$.cm), δ (55.2·I $kJmol^{-1}$) and *generalised parameters* α and β for salts (*3*:*1*) are 138.7 $kJmol^{-1}$.nm and 27.6 $kJmol^{-1}$, respectively. Equation (14) is normally employed for salts likely to have lattice energy greater than 5000 $kJmol^{-1}$ but it seems to work quite well in this case and for these materials.

C. Density:

One of the most important physical properties of energetic materials that are used to initially assess potential performance in a weapon is its density [9]. Important performance parameters such as the detonation performance (velocity and pressure) are proportional to density; the velocity increases linearly with density while the Chapman-Jouguet pressure (detonation pressure) is proportional to the square of the initial density (equations presented in next section). Density is a condensed phase property and its prediction involves challenges as it is associated with different intermolecular interactions, which affect the crystal pattern and cell volume. An increase in density is also desirable in terms of the amount of material that can be packed into volume-limited warhead or propulsion configurations. Therefore, substantial efforts have been directed toward developing a procedure that will accurately predict this property without a prior knowledge of the crystal structure. Some of the methods for a prediction of density are as 1. Group/volume additivity, 2. Quantum mechanical methods, 3. Crystal packing calculations, etc [10].

Group/volume additivity has the advantage of speed, low cost and ease of use; it is truly a fast procedure requiring only a list of appropriate atom and group volumes and a hand-held calculator. However, group additivity methods do not account for molecular conformation and isomerization. That is, it yields the same density values for different isomers or conformations of the same compound or even for different compounds with the same functional group composition, and ignores the density differences due to crystal polymorphism. In addition, inter and intra-molecular interactions and hydrogen bonding in the compounds are not accounted in group additivity methods. Quantum mechanical methods are widely used for the prediction of densities. Studies have indicated that, when the average molar volume (V) estimated by the Monte Carlo method based on 0.001 electrons/bohr^3 density space, the theoretical molecular density ($\rho = M/V$, where M is the molecular weight) is comparable to the experimental crystal density. Density functional theory (DFT) with different basis sets and various semiempirical molecular orbital (MO) methods have been employed to predict the molecular volumes of acyclic, monocyclic, and polycyclic molecules. Reliability of this method was demonstrated by experimental verification of the calculated data, which seems to be of essential interest and significance. Comparisons between the calculated and experimental densities suggest that quantum mechanical method is economical for predicting the solid-state densities of the organic nitramines, (especially for the monocyclic) but the densities of the compounds containing the fluorine element are all overestimated. Further, the densities predicted by the semiempirical MO methods are all systematically larger than the experimental ones.

Molecules tend to exhibit polymorphism, that is, they crystallize in many modifications, as a result of the physical conditions and the manner in which the crystals are obtained [11]. The structure of a molecular crystal is efficiently mathematically defined by specifying the content of the unit cell and the values of the unit cell parameters; that is, the lengths of the unit cell vectors (*a*, *b*, and *c*) and the angles between them (α, β, and γ). The content of the unit cell is specified by the coordinates of the asymmetric unit and by the space group. Therefore, to find the most probable crystal structures, it may at first appear that all possible space groups (230 in total) must be searched with different numbers of molecules in the asymmetric unit, a very time-consuming process. It is well known that among the 230 space groups quite a small fraction is typical of organic crystals. It has been found that over 80% organic compounds crystallizes in 10 typical space groups ($P2_1/c$, $P\text{-}1$, $P2_12_12_1$, $P2_1$, $C2/c$, $Pbca$, $Pna2_1$, $Pbcn$, Cc, and $C2$). Hence, the approach was based on the generation of possible packing arrangements in these space groups to search for the low-lying minima in lattice energy surface. The different force fields such as dreiding, pcff, compass, cvff, and universal can be used to predict the density. The possible crystal polymorph has been predicted using crystal packing calculations as implemented in polymorph module of the Material Studio. Most of the recent studies estimated the crystal densities using the crystal packing calculations and found superior over group additivity approaches and quantum mechanical methods.

D. Detonation performance (detonation velocity and detonation pressure):

The driving force behind the development of any new materials for the defence use is, and almost certainly will be, performance. Among the criteria used in evaluating potential energetic systems is detonation velocity and pressure for explosives, refer to the pressure and the rate of propagation of the shock wave front through the material. Detonation performance depends on the energy release that accompanies the decomposition and combustion processes occurring. Simple reliable prediction of the performance of notional energetic materials from a given molecular structure and the known or estimated crystal density is highly desirable to chemist for the expenditure connected with the development and synthesis of new and formulation of energetic materials. Prediction of the performance of new energetic materials should be evaluated prior to their actual synthesis because it reduces the costs associated with synthesis and test as well as evaluation of the materials.

Kamlet and Jacobs [12] estimated the detonation properties CHNO based energetic materials by means of relatively simple empirical equations. These equations imply that the mechanical properties of the detonation depend only on the number of moles of detonation gases per unit weight of explosive, the average molecular weight of these gases, the chemical energy of the detonation reaction, and the loading density. Explosive compound of composition, $C_aH_bN_cO_d$, in which there is at least enough oxygen to convert hydrogen to H_2O but no more than is also required to convert carbon to CO_2, the H_2O-CO_2 arbitrary calls for the formation of detonation products according to the following expression:

$$C_aH_bN_cO_d \longrightarrow 0.5c\ N_2 + 0.5b\ H_2O + (0.5d + 0.25b)\ CO_2 + (a - 0.5d + 0.25b)\ C$$

It follows then that,

$$N_{arb} = \frac{2c + 2d + b}{48a + 4b + 56c + 64d} \qquad (18)$$

$$M_{arb} = \frac{56c + 88d - 8b}{2c + 2d + b} \qquad (19)$$

$$Q_{arb} = \frac{28.9b + 47.0(d - b/2) + \Delta H^{o}_{f\ Explosive}}{12a + b + 14c + 16d} \qquad (20)$$

where in above equations, N_{arb} is the moles of gaseous detonation products per gram of explosives, M_{arb} is average molecular weights of gaseous products, Q_{arb} is chemical energy of detonation, a, b, c and d are the number of C, H, N and O in the compound and $H^0{}_f$ is the heat of formation of explosive. The empirical equations predicted to estimate the values of detonation velocity and pressure for the high energy materials containing CHNO as following equations:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_o) \qquad (21)$$

$$P = 1.55\rho_o{}^2\,(NM^{1/2}Q^{1/2}) \qquad (22)$$

where in above equations *VOD* is detonation velocity (kms^{-1}), *DP* is detonation pressure (GPa), N is moles of gaseous detonation products per gram of explosives, M is average molecular weights of gaseous products, Q is chemical energy of detonation ($kJmol^{-1}$) defined as the difference of the heats of formation between products and reactants, and ρ_o is the density of explosive (gcm^{-3}). Values of N, M, and Q estimated from the H_2O-CO_2 arbitrary decomposition assumption, so that the calculations require no other input information than the explosive elemental composition, heat of formation and loading density. Further, it is proved that detonation velocities and pressures calculated with Kamlet-Jacobs method are closer to experiment.

E. Oxygen balance (OB):

The oxygen balance (OB) is used to indicate the degree to which an explosive can be oxidized and oxygen is needed in a molecule to oxidize it completely into their gaseous reaction products. OB is used in prediction of detonation velocity, detonation pressure, chemical energy of detonation, and decomposition products. The molecule is said to have a positive (negative) oxygen balance if it contains more (less) oxygen than is needed for complete combustion. OB (%) for an explosive containing the general formula $C_aH_bN_cO_d$ with molecular mass *M* can be calculated as,

$$\mathrm{OB}(\%) = \frac{(d - 2a - 0.5b)}{M}\,\mathrm{X}\,1600 \qquad (23)$$

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Summary

and

Conclusions

The heterocyclic ring compounds are one of the interesting classes of compounds in high energy materials applications. Most of these compounds possess high heat of formation, velocity of detonation and detonation pressure. These superior properties make them more interesting and important in the area of explosives, propellants and pyrotechnics. If the heterocyclic molecules contain high nitrogen percentage in their backbone, they can be act as gas generators. These types of molecules are environmentally friendly and show differences in sensitivity to external stimuli. In view the developments in the field of nitrogen rich energetic materials; we projected our work to synthesize nitrogen rich energetic materials and their salts with variety of nitrogen containing ions (cations and anions).

In the present thesis work, we have synthesized several derivatives of heterocyclic compounds for potential high energy material applications. Most of the synthesized molecules are having good energetic properties. Some of the molecules are having more than 80% of nitrogen content in their backbone due to which they can be used as green energetic materials as well as gas generators. All of the synthesized compounds were characterized by NMR, IR, MASS and TG-DTA. Some of the compounds were characterized by single crystal X-Ray crystallography. In addition to the synthesis of these molecules, we have also calculated their energetic properties such as heat of formation, detonation velocity, detonation pressure and density through theoretical calculations.

Benzotriazole is a well-known fused heterocycle and is thermally stable due to its aromatic system. In ***chapter 2,*** we have described the introduction of different explosophores (nitro, azido, nitrate ester, etc.) were incorporated in benzotriazole to improve its energetic performance. Moreover, incorporation of azole rings into a compound is also a known strategy for increasing thermal stability. Hence, imidazole, pyrazole, triazole and tetrazole rings with various substituents are inserted in benzotriazole to enhance nitrogen content and oxygen balance. Overall, adding these functionalities to the benzotriazole ring typically altered the heat of formation making them more positive which is a desired characteristic for most energetic material. The calculated densities of the compounds ranged between 1.61 – 1. gcm^{-3}. The calculated detonation pressures (*DP*) for the benzotriazole derivatives fall in the range of 12.35 to 28.2 GPa, (comparable to the value of 19.5 GPa for TNT) and the detonation velocities (*VOD*) are distributed from 5.45 to 8.06 km/s (comparable to that for TNT, *D*=6.95 kms^{-1}). The energetic properties and thermal analyses of compounds **2.8-2.15** revealed that they have comparable performance to that for TNT which is bench mark explosive.

Chapter 3 presents the synthesis of nitrogen-rich imidazole, 1, 2, 4-triazole and tetrazole-based compounds. We mainly focused on tetrazole based materials as the tetrazole is a powerful building block for high energy density materials (HEDMs) due to its high nitrogen content (80%), high positive heat of formation (320 $kJmol^{-1}$), low sensitivity towards impact and good thermal stability due to its aromatic ring system. Among the designed compounds, **3.5** and **3.7** possess high positive HOFs (602 and 985 $kJmol^{-1}$, respectively) due to the presence of tetrazole ring. All the salts possess high positive HOFs, and salts of **3.11** have highest values due to significant energy contribution from **3.11** anion (610.7 $kJmol^{-1}$). The detonation parameters were calculated using Kamlet-Jacobs equations showed that the calculated detonation pressures (*DP*) were in the range14.7–27.2 GPa, and detonation velocity (*VOD*) were in between 6.0 and 7.85 kms^{-1}, which are more or less close to that of trinitrotoluene (TNT) (*DP* = 19.5 GPa, D = 6.8 kms^{-1}).

In Chapter 4, the 3,5-dinitropyridin-2-ol based energetic salts have been explored for their possible application as energetic materials Salts were prepared by combining 3,5-dinitropyridin-2-ol anion with urea, semicarbazide, carbohydrazide, biuret, guanidine, aminoguanidine, nitroguanidine, 1,3-diaminoguanidine, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 4-nitroimidazole, 3-nitro-1,2,4-triazole and 3,4-diaminofurazan as cations. All the salts were synthesized in simple and straight forward scheme with high yield achievable in the minimum number of steps. The calculated HOF values ranged from –583 to 51 $kJmol^{-1}$. With the exception of **4.12** (51 $kJmol^{-1}$), all salts possess negative heats of formation due to the negative HOF of the anion (-377 $kJmol^{-1}$) and high lattice energies. Densities for salts **4.1–4.13** found in the range between 1.60 and 1.74 gcm^{-3}. Among the designed salts, **4.7** and **4.12** possess highest densities of 1.71 and 1.74 gcm^{-3}, respectively. The calculated detonation velocities (*VOD*) ranged between 6.51 to 7.56 kms^{-1} and the detonation pressures (*DP*) fell in the range of 17.57 and 24.84 GPa. Most of these salts resulted in better performance over TNT.

In Chapter 5, we have presented the synthesis of energetic salts prepared from phenolate derivatives such as picric acid, 2,4,6-trinitro-m-cresol, 3-azido-2,4,6-trinitrophenol, styphnic acid (2,4,6-trinitrobenzene-1,3-diol), and 2,4,6-trinitro-1,3,5-benzenetriol. Nitrophenols have limited applications in energetic materials as they are known to react with surrounding metals to yield very sensitive compounds. We have extended our studies to understand structure-performance relationship with various cations in combination with phenolate anions having 1:1, 2:1 and 3:1 charge ratio. The typical cations used in these systems are, 4-amino-4H-1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 3,4-diaminofurazan and guanidine. Among the series of nitrophenol salts, the salts of 3-azido-2,4,6-trinitrophenol (**5.3b-5.3e**) possess highest HOFs attributed to the presence of azido group. The densities of most of the new salts ranged between 1.58 and 1.76 gcm^{-3}. The calculated detonation pressures of picric acid salts (**5.1a-5.1e**), styphnic acid (**5.4b-5.4e**) and 2,4,6-trinitrophloroglucinol (**5.5a-5.5e**) lie in the range between P=16.8 and P=24 GPa and detonation velocities (VOD) lie between 6.4 and 8 kms^{-1}. Comparing the performance characteristics of 2,4,6-trinitro-m-cresol (**5.2a-5.2e**) and 3-azido-2,4,6-trinitrophenol (**5.3b-5.3e**) salts reveals that 3-azido-2,4,6-trinitrophenol salts possess better performance due to their high densities. All salts appear to be sufficiently thermally stable, their decomposition temperatures found in the range 231-291 °C, while their melting points lie between 110-241 °C. Overall, all the phenolate salts exhibited good thermal stabilities, better densities, reasonable detonation pressures and detonation velocities.

In Chapter 6, we have further extended or study to salta having tetra anoion and four cations (4:1 charge ration). We have discussed the synthesis, characterization and energetic properties of nitrogen-rich energetic tetraanionic salts of 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane (TTP) [7]. Reactions of TTP with 4 molar equivalents of imidazole, 4-nitroimidazole, 4-amino-4*H*-1,2,4-triazole, 1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 3-nitro-1,2,4-triazole, 3,4-diaminofurazan, 5-aminotetrazole, melamine, 2,4,6-trinitroaniline, and guanidine in methanol resulted in the formation of the target tetraanionic salts **6.1-6.12**. The calculated HOF of TTP (1045 $kJmol^{-1}$) was more positive and can be attributed to the high energy contribution from the four tetrazoles. HOFs exhibited by these energetic salts were in the range of 319–1984 $kJmol^{-1}$. The densities of salts **6.1–6.12** fall in the range of 1.49–1.71 gcm^{-3}. Presence of the nitro group played an important role in increasing the density and hence, **6.7** and

6.11 possessed the highest densities at 1.71 and 1.70 gcm^{-3} respectively. The detonation velocities ranged between 5–8 kms^{-1} and detonation pressures (*DP*) lied between 10–25 GPa. Salts **6.7** (*VOD* = 7.53 kms^{-1}, *DP* = 24.41 GPa) and **6.11** (*VOD* = 7.51 kms^{-1}, *DP* = 24.13 GPa) exhibited better detonation performance than the TNT (*VOD* = 7.21 kms^{-1}, *DP* = 22.49 GPa). Overall, TTP salts possess high nitrogen content, high positive HOFs, and moderate performance.

Altogether, we have synthesized about 150 compounds/salts and valuated their energetic properties for potential use as high energy density materials (HEDMs). Among these compounds we have identified best five compounds (which are listed in the table SC-1) based on properties and ease of synthesis for scale-up of synthesis and real-time performance evaluation.

Table SC-1: Calculated energetic properties of sew selected compounds

Compound	*Density (gcm^{-3})*	*M.p (°C)*	*T_{dec} (°C)*	*OB (%)*	*$\Delta_f H$ (Calg^{-1})*	*VOD (kms^{-1})*	*DP (Gpa)*	*Cumulative yields (%)*
2.7	1.77	decompose	150	- 57.6	540	6.48	18.28	50
2.11	1.81	decompose	168	- 70.0	332	7.65	26.03	40
TTP	1.64	decompose	276	-91.1	790	6.63	18.43	70
6.7	1.71	212	226	- 62.1	594	7.53	24.41	80
6.11	1.70	190	260	- 65.1	348	7.51	24.13	80
TNT	1.68	--	--	-74.0	-295	7.20	22.48	--
RDX	1.82	204	230	-21.0	89	8.75	34.90	--
HMX	1.91	276	280	-21.0	75	9.10	44.60	--

As far as I can say, this thesis contains useful information and compounds, some of them under current investigation as applied energetic materials, and some of them bearing the potential of possibly serving as roadmap towards next generation energetic materials.

List of Acronyms

RDX	1,3,5-trinitro-1,3,5-triazinane
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocane
TATB	Triaminotrinitrobenzene
NTO	3-Nitio-l, 2, 4-triazol-5-one
HNS	Hexanitrostilbene
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
N-60	Nitrogen Fullerene which contains 60 Nitrogen atoms
AP	Ammonium perchlorate
AN	Ammonium nitrate
ADN	Ammonium dinitramide
MTNP	Methyltrinitropyrazole
MTNI	methyltrinitroimidazole
ATz	Aminotetrazole
ATTz	6-amino-tetrazolo[1,5-b]-1,2,4,5-tetrazine
ANTz	4-amino-5-nitro-1,2,3-triazole
TNM	Tetranitromethene
GAT	Guanidiniumazotetrazolate
DHTz	3,6-dihydrazinyl-1,2,4,5-tetrazine
BTATZ	N3,N6-di(1*H*-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine
TNAZ	1,3,3-trinitroazetidineTNCB 1,1,3,3-tetranitrocyclobutane
HEMs	High energy materials
HOF	Heat of formation
VOD	Velocity of detonation
DP	Detonation pressure

List of Publications

Publications from thesis

1. "Synthesis of Amino, Azido, Nitro and Nitrogen-rich Azole Substituted Derivatives of 1*H*-Benzotriazole for High Energy Materials Applications",

   D. Srinivas, V. D. Ghule, S. P. Tewari, and K.Muralidharan, *Chem. Eur. J.* **2012**, *18*, 15031-15037.

2. "Tetraanionic nitrogen-rich tetrazole based energetic salts",

   D. Srinivas, V. D. Ghule, K. Muralidharan, H. Donald B. Jenkins, *Chem. Asian J.* **2013**, *8*, 1023-1028.

3. "Energetic Monoanionic Salts of 3,5-Dinitropyridin-2-ol",

   Vikas D. Ghule, **D. Srinivas,** K. Muralidharan, *Asian J. org. chem.* **2013**, *8*, 662-668.

4. "Synthesis of nitrogen-rich imidazole, 1,2,4-triazole and tetrazole-based compounds",

   D. Srinivas, Vikas D. Ghule, K. Muralidharan, *RSC Adv.* **2014,** *4*, 7041-7051.

5. "Energetic Salts Prepared from Phenolate Derivatives"

   D. Srinivas, Vikas D. Ghule, K. Muralidharan, *New J. Chem.*, **2014,** *38,* 3699-3707.

Other publications

1. "Computational study on energetic properties of nitro derivatives of furan substituted azoles",

   V. D. Ghule, **D. Srinivas,** S. Radhakrishnan, P. M. Jadhav, S. P. Tewari, *Struct. Chem.* **2012**, *23*, 749-754.

2. “Molecular design of amino-polynitroazole based high energy materials”, V. D. Ghule, **D. Srinivas,** S. Radhakrishnan, P. M. Jadhav, S. P. Tewari, *J. Mol. Model.* **2012**, *18*, 3013-3020.

3. “Kinetics of proton transfer dissociation in tetrazole based nitrogen-rich Tetraanionic energetic salts and their temperature dependent decomposition mechanism”, **D. Srinivas,** Anuj A. Vargeese, K. Muralidharan, **2014** (under review)

Poster and Oral Presentations

1. Dharavath Srinivas, 8th International High Energy Materials Conference and Exhibit (HEMCE-2011), Terminal Ballistics Research Laboratory (**TBRL**), **10-12 Nov. 2011,** Chandigarh, India.

2. Dharavath Srinivas, International Symposium on Recent Trends in Spectroscopy and Dynamics of Chemical Systems, **7-8 Dec. 2011**, University of Hyderabad, Hyderabad. India.

3. Dharavath Srinivas, 'Modern Trends in Inorganic Chemistry (MTIC-2012)' held at University of Hyderabad, on **Feb 13-14, 2012.**

4. Dharavath Srinivas, 'Andhra Pradesh Science Congress', **14-16 Nov. 2013,** University of Hyderabad, India on Mar 03-04, 2012.

5. Dharavath Srinivas and Krishnamurthi Muralidharan, presented a poster in In-house symposium, School of Chemistry, University of Hyderabad on **2013.**

6. Dharavath Srinivas, Participated in UGC Networking program on Computation Chemistry, **02-14 Dec. 2013,** University of Hyderabad, Hyderabad. India.

7. Dharavath Srinivas and Krishnamurthi Muralidharan, presented a poster in In-house symposium, School of Chemistry, University of Hyderabad on **2014**.

8. Dharavath Srinivas and Krishnamurthi Muralidharan, 9th International High Energy Materials Conference and Exhibit (HEMCE-2014), Vikram Sarabai Space Centre (**ISRO**), **13-15 Feb. 2014,** Thiruvananthapuram, India.

9. Dharavath Srinivas won **Dr. K. V. Rao Young Scientist award for the year of 2013-14.**

I learned during this four years:

"You cannot invent a new world. However, you can improve it! And you can also love it!"